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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

THE STRUCTURAL PECULIARITIES OF LIQUID ALLOYS IN CERTAIN BINARY SYSTEMS

D. K. Belashchenko

(Presented by Academician G. V. Kurdyutov, April 25, 1957)

In this work, the attempt is made to measure and compare various physical properties of liquid alloys in certain binary systems and to determine the most probable characteristic features of the short-range order in the corresponding liquids. We have established certain regularities in the influence of the electron concentration on the properties of the liquid alloys, in the relationship between the thermodynamic and kinetic properties of the latter and in the relation between the structures of the alloys in the liquid and in the solid conditions.

The viscosity and the electrical resistance were chosen as "structurally sensitive" liquid properties. In Figure 1 is shown a sketch of the apparatus with which measurements of these properties were carried out.

The technique employed by us was a combination of the method of determining the kinematic viscosity from the damping of the torsional vibration of a cylindrical crucible filled with the liquid and suspended on an elastic filament [1] and the method of determining the electrical conductivity from the angle of twist of a specimen in a rotating magnetic field [2]. The apparatus permitted the determination of the viscosity and the electrical resistance in the course of a single experiment. The rotating magnetic field was generated by three pairs of coils located on the external surface of the housing of the apparatus. The heating element was a graphite tube surrounded by a layer of thermal insulation (carbon black). The electrical resistance was determined from the twist angle, α, as indicated by a light ray reflected from a spherical mirror affixed to the suspension. The kinematic viscosity was determined from the decrement of the damping of the free torsional vibration of the crucible with the metal. The random error of measurement of the viscosity amounted to $\sim 2\%$.

Binary systems were selected on the basis of their phase diagram types. In this connection, liquid alloys were investigated in the systems Sb-Sn (a liquidus curve monotonically rising from Sn to Sb), Cd-Sb (in the phase diagram there is present a stable intermetallic compound, CdSb, and a metastable compound, Cd_3Sb_2, which crystallizes during the cooling of melts), Cd-Cu (an electronic compound with the γ-brass structure exists and there is a corresponding maximum on the liquidus curve), Pb-Tl (a diagram with a very flat maximum on the liquidus curve), Bi-Tl (a liquidus curve with two maxima) and Fe-Ni (complete solubility in the solid state at high temperatures).

In this work we used spectrally pure tin, antimony with traces of iron, cadmium with traces of copper, spectrally pure lead, thallium with traces of copper and silver, bismuth with traces of copper, electrolytic copper, iron, and nickel. All of these experiments were performed in a atmosphere of hydrogen. The pure metals with the exception of nickel, copper, antimony and iron, and the alloys with the exception of those of iron and nickel, were prepared by mutual fusion in hydrogen, with subsequent filtration through porous glass filters under pressure. Filtration was resorted to in order to remove from the liquid various insoluble contaminants which markedly affect the viscosity.

In Figure 2, isotherms are presented which show the dependence on concentration of the kinematic viscosity ν and the electrical resistance ρ' (in relative units) of those liquid alloys in the Cd-Sb system which crystallizes according to the metastable phase diagram. The viscosity isotherms each have a maximum in the concentration range 40-50 at. % Sb, clearly marked at 450-550°C and gradually levelling out with elevation of the temperature. By lowering the temperature, the maximum in ν is displaced from 50 at. % Sb toward smaller Sb concentrations, i. e., toward the Cd_3Sb_2 composition. At 50-80% Sb, the liquid Cd-Sb alloys possess anomalous thermal coefficients of electrical resistance.

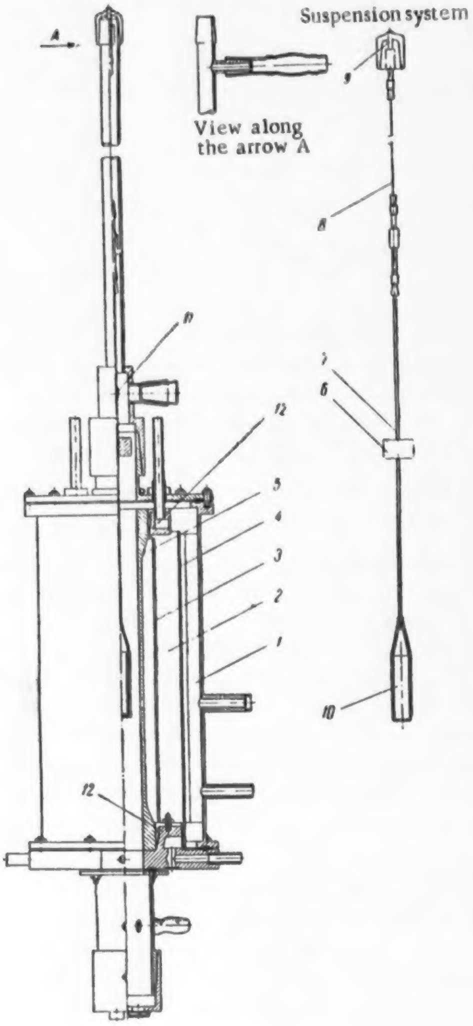

Fig. 1. A sketch of the apparatus for measuring the viscosity and the electrical conductivity of liquid metals.

1) Coil stator, 2) thermal insulation, 3, 4) graphite screens, 5) heating tube (graphite), 6) weight, 7) suspension, 8) tungsten wire, 9) glass joint with sealed in molybdenum spindle, 10) crucible, 11) spherical mirror, 12) electrical leads.

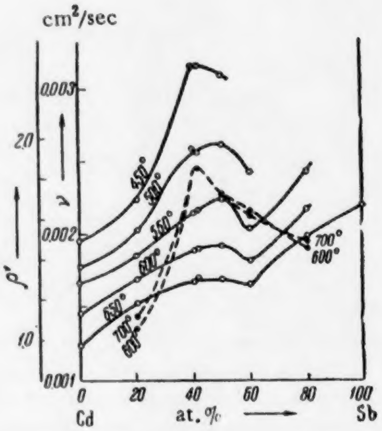

Fig. 2. Isotherms of the kinematic viscosity, ν, (full curves) and the specific resistance, ρ', (dotted curves) of liquid alloys in the Cd-Sb system.

These data permit the supposition that alloys near CdSb continue after fusion to retain in the liquid phase that atomic packing which approximates the structure of the compound CdSb, this latter progressively dissociating as the temperature is elevated.

From the data presented it can also be concluded that the state of the liquid Cd-Sb alloys which results from cooling differs from that resulting from a preceding heating. The displacement of the maximum of ν from 50% to 40% Sb during melt cooling indicates that even in the liquid state there occur the mutual regroupings of the particles which lead to the crystallization of the compound Cd_3Sb_2. This statement is in accordance with the pronounced hysteresis in the viscosity of the alloy with 50 at.% Cd and, to a lesser degree, in the alloy with 60 at. % Cd (Fig. 3; a, b) during cooling the viscosity runs somewhat higher than during heating. This phenomenon is possibly similar in principle to that of the branching in the relation between the viscosity of pure tin and the temperature [3].

Hysteresis is also to be observed with the liquid alloys from the systems Pb-Tl and Bi-Tl. All of these alloys crystallize with supercooling. The curves showing the viscosity of alloys of Pb with 20, 40 and 80 at.% Tl fall lower during cooling than during heating (the alloy with 60% Tl does not show hysteresis). Pure thallium behaves very peculiarly (see Fig. 3, c); the viscosity curve for Tl has a low maximum in the region 350-450° (the electrical conductivity increases with

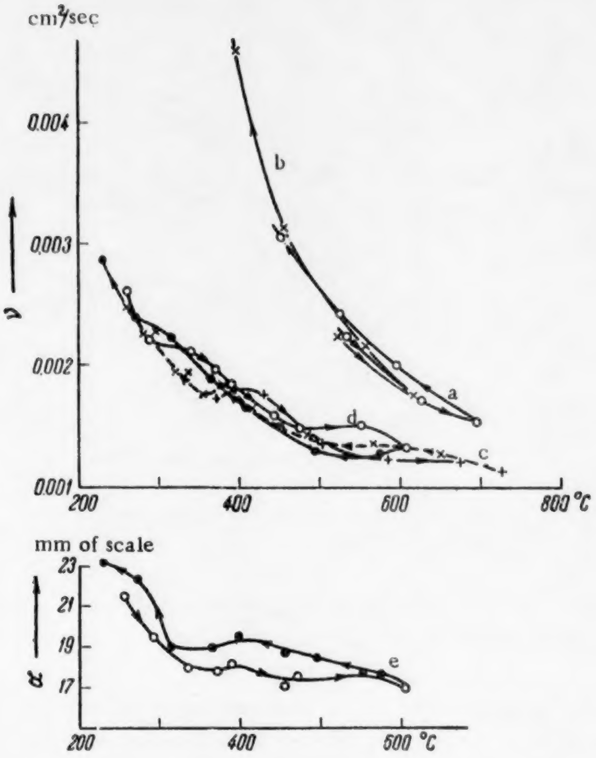

Fig. 3. The kinematic viscosity of liquid alloys in the Cd-Sb system: a) 60 at.% Cd, b) 50 at.% Cd; c) the kinematic viscosity of pure thallium; d) the kinematic viscosity ν and e) the angle of twist α (in relative units) of an alloy of Bi with 73% Tl in a rotating magnetic field.

temperature) and an inflexion point at 600-650°C. These peculiarities are reproduced on recooling the specimen. It can be supposed that in liquid thallium at 350-400°C there occurs a change in the short-range order, this involving a relative increase in the viscosity and the electrical conductivity during heating and the reverse processes during cooling. This process affects the properties of the alloys with thallium. In particular, alloys of Tl and Bi show an anomalous course for the viscosity and for the electrical resistance around 350-400°, just as in the case of pure thallium, and these anomalies smooth out with decreasing content of Tl. The second anomaly, in the region 500-600°, is no longer observable in alloys with 55.5% Tl and less. In alloys with 72% and 89% Tl this latter takes on a curious form: by heating above 500° and then recooling, the graph of $\nu(T)$ forms a "loop" (Fig. 3, d); the electrical conductivity is higher during cooling than it is during heating (Fig. 3, e). A dependence of the properties of liquid Bi-Tl alloys on time is found only in the region of this "loop". By holding an alloy with 72% Tl at a temperature of 650-670° there was disclosed a diminution of the viscosity and the electrical resistance; this process has an asymptotic character, the relaxation time being of the order of 1 hour. In subsequent slow coolings and heatings these anomalies are no longer detectable.

The results which have been presented make it possible to consider that in a number of cases there are possible liquid states which are metastable with respect to other states of the given liquid and are stable over more or less extended periods of time. It should be noted that in all of the investigated cases, hysteresis in the liquid alloys was accompanied by a tendency toward supercooling.

The viscosity and the electrical resistance of liquid alloys in the system Cd-Cu change non-monotonically with the concentration; monotonic change is observed with 30-40 at. % Cu, i. e., above the electronic compound

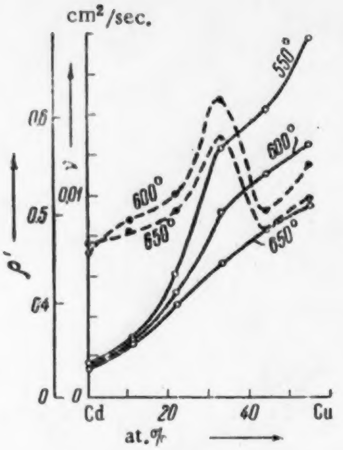

Fig. 4. Isotherms of the kinematic viscosity ν (full curves) and the specific resistance ρ' (dotted curves) of liquid alloys in the system Cd-Cu.

Cd_8Cu_5 (δ-phase) (see Fig. 4, dotted curve of relative electrical resistance). These phenomena are related to the relatively weak dissociation of the γ-brass structure during fusion (in distinction to electron compounds of the second type).

In the systems Pb-Tl, Bi-Tl and Cd-Sb the form of the viscosity isotherms strongly recalls that of the curves of the beginning of solidification. In the systems Sb-Sn and Fe-Ni the situation is, in general, the same, although at equiatomic concentrations there appears a tendency for the value of the viscosity of the alloy to approach the mean of the viscosities of the components. Thus the viscosity isotherms for Sb-Sn alloys have two maxima with an intermediate minimum, while the viscosity isotherms of Fe-Ni alloys have two maxima with an intermediate minimum, while the viscosity isotherms of Fe-Ni alloys have two minima. These tendencies are also to be observed in the system Bi-Tl.

The I. V. Stalin Steel Institute, Moscow

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THE POTENTIAL DIFFERENCE AND THE ACCUMULATION OF THE COMPONENTS OF A SOLUTION IN THE DIFFUSION LAYER DURING STATIONARY ELECTROLYSIS

Academician A. N. Frumkin

It is the purpose of the present communication to direct attention toward certain peculiarities in the distribution of the concentration and potential in the diffusion layer during stationary electrolysis. Despite the fact that a correct treatment of the special case of a solution containing univalent ions at a dilution permitting an application of the laws of ideal systems was given by Eucken fifty years ago [1], this problem has in the sequence not been given adequate attention. We will first consider the case of the stationary electrolysis of a binary electrolyte, consisting of a discharging cation of charge n_1 and a nondischarging anion of charge n_2, at an arbitrary concentration. The activities of the respective ions in the body of the solution beyond the limits of the diffusion layer we will designate by a_1' and a_2' and will consider these to be the same at all points of the solution; the activities in the diffusion layer in the immediate neighborhood of the electrode surface will be designated by a_1'' and a_2''. Since the nondischarging anions are stationary, it follows from the Boltzmann equation that under stationary conditions

$$\Phi = \frac{RT}{n_2F} \ln \frac{a_2''}{a_2'}, \tag{1}$$

where Φ is the difference in potential between points on the surface of the electrode and in the body of the solution.

At first sight it would seem that Equation (1) would permit the determination of the quantity a_2''/a_2' and, accordingly, allow a comparison of the values of the activity of the individual ion at any concentration. Such a conclusion would, however, be in error since it is not the quantity Φ which is open to direct measurements but rather the sum $\Phi + \Delta\varphi$, where $\Delta\varphi$ is the alteration in the electrode-solution potential difference, φ, which results from a change in the concentration in the pre-electrode layer (concentration polarization, in the usual sense of this word).* If it is supposed that the electrode is reversible with respect to the discharging cation then

$$\Delta\varphi = \frac{RT}{n_1F} \ln \frac{a_1''}{a_1'},$$

from which it follows that

$$\Phi + \Delta\varphi = \frac{RT}{F} \ln \left(\frac{a_1''}{a_1'}\right)^{\frac{1}{n_1}} \left(\frac{a_2''}{a_2'}\right)^{\frac{1}{n_2}} = \frac{1}{n_1n_2} \frac{RT}{F} \ln \frac{a''}{a'} = \frac{n_1+n_2}{n_1n_2} \frac{RT}{F} \ln \frac{a_\pm''}{a_\pm'}. \tag{2}$$

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* Here it is supposed that the ohmic fall of potential in the body of the solution beyond the limits of the diffusion layer has been eliminated, either by calculation or through direct measurement, which, in principle, is always possible.

a being the activity of the electrolyte molecule, $a_\pm$ the mean activity of its ions and the indices (' and ") retaining their original significance. It follows from Equation (2) that the quantity $\Phi + \Delta\varphi$, which is open to measurement, is expressed through the mean activities rather than through the individual activities of the separate ions. So far as is known to the author, Equation (2) has not as yet been subjected to experimental verification, even for the simplest case of the dilute solution.* Much interest would attach to the application of Equation (2) to concentrated solutions such as acids. In this case the combination of a determination of the magnitude of $\Phi + \Delta\varphi$ using the reversible hydrogen electrode as the cathode, with a direct determination of the distribution of the electrolyte concentration in the diffusion layer such as could be carried, for instance, by interferometer methods, would make it possible to fix the activity in concentrated solutions.

We will now consider the case of a dilute solution containing discharging cations 1 with a charge n_1 at a concentration c_1 (in equivalents per cm^3) and the nondischarging anions 2 and cations 3 with charges n_2 and n_3 at concentrations c_2 and c_3. According to the condition of electral neutrality

$$c_1 + c_3 = c_2. \tag{3}$$

Between the concentrations of the nondischarging ions at the electrode surface (c_2'', c_3'') and in the body of the solution beyond the limits of the double layer (c_2', c_3') there exists during stationary electrolysis the relations

$$c_2'' = c_2' \exp\left(\frac{n_2\Phi F}{RT}\right), \tag{4}$$

$$c_3'' = c_3' \exp\left(-\frac{n_3\Phi F}{RT}\right), \tag{4a}$$

from which it follows that

$$c_1'' = c_2' \exp\left(\frac{n_2\Phi F}{RT}\right) - c_3' \exp\left(-\frac{n_3\Phi F}{RT}\right), \tag{5}$$

c_1'' being the value of c_1 at the electrode surface.

On reaching the limiting current, $c_1'' = 0$, and, accordingly,

$$\Phi = \frac{RT}{(n_2+n_3)F} \ln \frac{c_3'}{c_2'}, \tag{6}$$

$$c_3'' = c_3'\left(\frac{c_2'}{c_3'}\right)^{\frac{n_3}{n_2+n_3}} = (c_3')^{\frac{n_2}{n_2+n_3}} (c_2')^{\frac{n_3}{n_2+n_3}}. \tag{7}$$

Definite interest attaches to the case where $c_3' \ll c_1', c_2'$ and consequently, $c_1' \approx c_2'$.

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* In a solution of a uni-univalent electrolyte ($n_1 = n_2 = 1$) the coefficient preceding the logarithm reduces to 2. From this it follows that the slope of the curve $-\varphi$, against $\ln \frac{I_d - I}{I}$ (where I is the current strength and I_d is the strength of the limiting diffusion current) must, in the case of the reversible cathodic formation of an amalgam, have a value which is twice as great as that observed in the presence of an excess of an indifferent electrolyte. The difficulties of an experimental confirmation are related to the relatively high ohmic drop in the potential in the body of the solution beyond the limits of the diffusion layer in the absence of an electrolyte background; they may, however, as calculations show, be overcome if the diameter of the cathode is sufficiently small (for example $\sim 5 \cdot 10^{-3}$ cm) and the depth of the diffusion layer sufficiently great ($\sim 10^{-1}$ cm); this can be easily realized by utilizing a mercury meniscus in a capillary as the cathode.

$$\frac{c_3''}{c_3'} = \left(\frac{c_1'}{c_3'}\right)^{\frac{n_3}{n_2 + n_3}} . \qquad (8)$$

With $c_1'/c_3' = 10^4$, $n_3 = 3$ and $n_2 = 1$, the degree of concentrating of the nondischarging cation as expressed by the right member of Equation (8), amounts to 10^3. The practical applicability of this method of increasing the concentration is limited by the fact that the time, τ, required for establishing a stationary concentration distribution in the diffusion layer, rises in proportion to the increase of the depth, l, of the latter. Since according to order of magnitude

$$\tau \approx \frac{l^2}{D} ,$$

it then follows that with $l = 0.1$, $\tau \approx 10^3$ sec., and with $l = 1$ cm, $\tau = 10^5$ sec. Analytical applications of this increase in concentration are, however, significant. Thus, for example, if the cation which is present as an additive is nondischargeable at the potential under which stationary electrolysis is being carried out but can be discharged at a more negative potential, the accumulation of it in the diffusion layer with the separation of a base metal can be employed for subsequent oscillographic polarography. The accumulation of a surface organic cation at the surface of a hanging mercury droplet during cathodic precipitation of the cation of the background could be disclosed by subsequent measurement of the interfacial tension at the mercury-solution boundary.

The quantity Φ in Equation (6) is usually designated as the ohmic potential drop in the diffusion layer. It should, however, be recalled that this is not equal to the potential drop as calculated from Ohm's law using the specific resistance and current density in a column of electrolyte of varying concentration which is the diffusion layer, but differs from this in the direction of an EMF which is equal to the diffusion potential arising in that same column, in the absence of a current, because of differences in the ionic mobilities. This was proven earlier for the case of a binary electrolyte [2].

In view of the fact that the theory of this question is frequently incorrectly developed, it will be useful to illustrate the relationship between the total and the "ohmic" fall in potential in the diffusion layer for the case of an electrolyte with three ions. Here we will for simplicity in the calculations set all of the $\underline{n}$ equal to unity and we will suppose, in distinction from the example which has just been treated, that the concentration of the discharging ion, c_1, is small in comparison with the concentrations of the nondischarging anions and cations, c_2 and c_3. From this it follows that $c_2 \approx c_3 \approx c$, $\underline{c}$ designating the concentration of the background.

From (6) and (3) it follows that for the case under consideration

$$\Phi = \frac{RT}{2F} \ln \frac{c_2' - c_1'}{c_2'} = - \frac{RT}{2F} \frac{c_1'}{c_2'} = - \frac{RT}{2F} \cdot \frac{c_1'}{c'} . \qquad (9)$$

We will compare this quantity with the potential drop in the diffusion layer, Φ_{ohm}, as calculated according to Ohm's law from the current density, $\underline{j}$, and the resistance, $\underline{r}$, of the electrolyte per 1 cm^2 of surface. The magnitude of j is equal to $\frac{FD_1c_1^1}{l}$, D_1 being the diffusion coefficient for the cations 1, and l the depth of the diffusion layer. Replacing D_1 through the mobility U_1, using the Nernst equation, we obtain

$$j = RT \frac{U_1 c_1'}{l} . \qquad (10)$$

Since at all points of the layer the concentration c_1 is small in comparison with $\underline{c}$, $\underline{r}$ is approximately equal to $l : c' (U_2 + U_3) F$, where U_2 and U_3 are the mobilities of the anion 2 and the cation 3. From this we obtain

$$\Phi_{ohm} = -rj = -\frac{RT}{F}\frac{c_1'}{c'}\frac{U_1}{U_2+U_3}. \tag{11}$$

Comparing (9) and (11) it is to be seen that $\Phi \neq \Phi_{ohm}$. From Equations (7) and (9) it follows for the case in which $n_2 = n_3 = 1$ and $c_1/c_3 \ll 1$, that

$$c_3'' \approx c_2'' \approx c_3' + {}^1/_2 c_1' = c_2' - {}^1/_2 c_1'. \tag{12}$$

Since the fall in concentrations in the diffusion layer is small in the case under consideration, the magnitude of the diffusion potential Φ_D arising in this layer can be calculated from the equation of Henderson [3], using the values of the concentrations and mobilities at its surface and taking no account of the distribution of concentrations within the layer. For a small fall in concentration, we find from the Henderson equation, Equation (12) and the conditions $c_3'' = 0$, $c_1' \ll c'$, $c_2' \approx c_3' \approx c'$ that

$$\Phi_D = -\frac{RT}{F}\frac{U_1(c_1'' - c_1') - U_2(c_2'' - c_2') + U_3(c_3'' - c_3')}{U_1 c_1' + U_2 c_2' + U_3 c_3'} = \frac{RT}{F}\frac{c_1'}{c'}\left(\frac{U_1}{U_2+U_3} - \frac{1}{2}\right). \tag{13}$$

From Equations (9), (11) and (13) we obtain the result $\Phi = \Phi_{ohm} + \Phi_D$, just as would be expected.

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* In Russian.

THE ELECTROCHEMICAL PRINCIPLES OF THE PROTECTION OF METALS IN STRONG OXIDIZERS

V. P. Batrakov

(Presented by Academician S. I. Volkovich, May 11, 1957)

At the present time it has been established that the high rate of corrosion of many metals and alloys in strong oxidizing agents is related to the overpassivity, i. e., to the destruction of the protective films or to the weakening of their protective properties because of the high oxidation-reduction potential resulting from the formations of ions or soluble metallic compounds of higher valence [1-6].

A schematic polarization diagram for metals in the overpassive condition is shown in Fig. 1. At high potentials the anodic polarization of the metal sharply diminishes and the curve 1 showing the anodic polarization takes on a more sloping course so that the rate of self-dissolution of the metal increases (I_{ov}) [4]. The protection of metals under these conditions involves either the decrease of the potential to a value under which stable passivity arises (this potential must lie between the first and second critical potentials) [5, 6], or the strengthening of the surface film so as to render difficult the high potential anodic processes, i.e., so as to increase the film's protective properties [4]. In conformity with what has been said, the following should be included among the basic methods of metal protection at overpassivity.

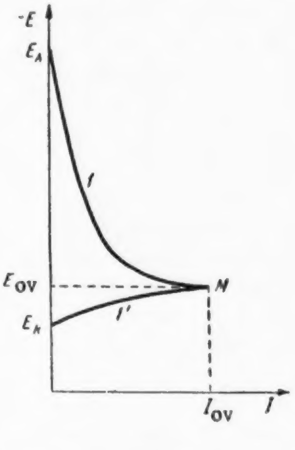

Fig. 1. A polarization diagram explaining the mechanism of metal corrosion at overpassivity.

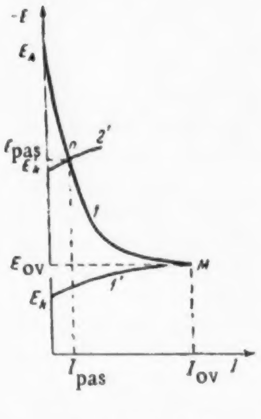

Fig. 2. A polarization diagram explaining the mechanism of protecting metals at overpassivity by means of a diminution of the oxidation-reduction potential of the medium.

1. Diminishing the oxidation-reduction potential of the medium. By decreasing the oxidation-reduction potential of the medium from E_k to E_k', the curve 2' of cathodic polarization, in distinction to the curve 1',

cuts the curve of anodic polarization 1, on a segment which is characterized by passivity of the metal. The magnitude of the stationary potential and the local current strength are thereby decreased from E_{ov} to E_{pas} and from I_{ov} to I_{pas} (Fig. 2). The metal passes from an overpassive state into a condition of stable passivity. A diminution of the oxidation-reduction potential of the medium can be brought about by decreasing the concentration of the the oxidizing agent or by the addition of a reducing agent [2, 5, 7].

This method of protection can not always be employed since it involves a decrease of the oxidizing properties of the medium and a change in the composition of the latter.

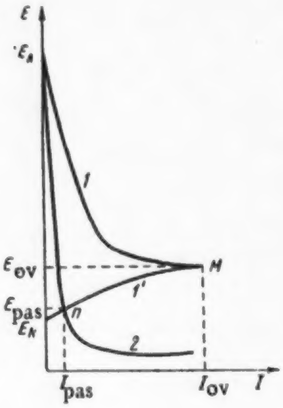

Fig. 3. A polarization diagram explaining the mechanism of protecting metals at overpassivity by means of an increase in the overvoltage of the anodic process.

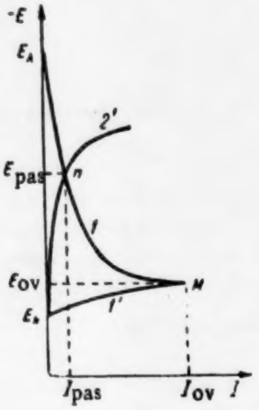

Fig. 4. A polarization diagram explaining the mechanism of protecting metals at overpassivity by means of an increase in the overvoltage of the cathodic process (cathodic passivity).

2. Increasing the overvoltage of the anodic process. An increase in the overvoltage of the anodic reaction can be brought about by a strengthening of the surface film, as a result of which the curve of anodic polarization will be characterized by a steeper course. The effect of overpassivity appears in this case at considerably higher potentials (Fig. 3, 2) and results from an increase of the overvoltage for the formation of ions or metallic compounds of higher valence. The oxidizing properties of the solution are thereby retained unchanged. The curve of cathodic polarization, 1', will intersect the curve of an anodic polarization, 2, in contrast to the anodic curve 1, on a section which is characterized by the passive state of the metal. As a result of this, the strength of the corrosion current is diminished from I_{ov} to I_{pas} (Fig. 3) [4]. The stationary potential of the metal is thereby somewhat raised and reaches the value E_{pas}. The increase of the protective properties of the film can be achieved by any one of the following: a) by a suitable alloying with elements which increase the overvoltage of the anodic reaction; b) by the introduction of surface active substances, the anodic corrosion retarders, into solution; c) by a decrease of the internal strain in the metal and the film, through suitable thermal working.

In all of these cases the anodic polarization sharply increases and the metal remains in a stable passive stage at high potential. The surface active substances are either adsorbed or form difficultly soluble surface compounds, which strengthen the protective film on the metal.

3. Increasing the overvoltage of the cathodic process. This method of protection is in principle different from those methods which have been considered above. The decrease in the potential of the metal is achieved in this case, not by diminishing the oxidizing properties of the solution (Fig. 2), but by increasing the overvoltage of the cathode reaction. The stationary potential of the metal is thereby lowered to a value at which a stable passive condition is reached (cathodic passivity) [5, 6]. The corrosion current is lowered from I_{ov} to I_{pas} (Fig. 4). A strong cathodic polarization can be achieved by:

a) suitable alloying with elements which raise the overvoltage of the cathode reaction;

b) introducing surface active substances (cathodic corrosion inhibitors) into solution;

c) cathodic protection and protection by a protector in the case of the formation of a protective film by cathodic polarization (cathodic passivity).

In addition to the methods of protection which have been considered, combination of these methods can be very effective. Cathodic protection and protection by a protector under conditions of overpassivity can also be considered within the usual scheme of electrochemical protection, i. e., without taking into account the formation of protective films on the metal.

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AN APPLICATION OF THE EMANATION METHOD TO THE INVESTIGATION OF CATALYSTS

THE TOPOCHEMICAL DECOMPOSITION OF THE CARBONATES AND HYDROXIDES OF MAGNESIUM AND ZINC

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The catalytic activity of solid bodies is closely related to the structural defects in their crystal lattices. These defects arise during the genesis of the catalyst and are in number and character determined by the mechanism and the microchemistry of the topochemical steps in the preparation. These processes are closely tied up with the displacement of separate atoms, or groups, in the lattice of the solid body and on its surfaces, and frequently escape the ordinary physical methods of investigation. The prospect is presented of applying for their study the emanation method proposed by Kolovrat-Chervinsky[1]. In the works of Hahn, Starik, Tsimens and many others, there has been pointed out the possibility of using this method to disclose hidden phase changes and chemical transformations in solid bodies, as well as variations in the mobility of the atoms in the lattice, the specific surface and the porosity [2-5].

The various systems which have been studied by the emanation method are of interest for catalysis, although it is obvious that, up to the present, the method has not been applied in catalytic studies. We have decided to fill up this gap by utilizing measurements of emanating power for investigating the topochemical stages in the preparation of oxide catalysts and the transformations to which these are subjected during treatment.

Of the three isotopes of radium (Ra, ThX, AcX) which generate those isotopes of the element 86 which are employed in the emanation method, we have utilized Ra 226 in the form of a nitrate solution with a concentration of $3 \cdot 10^{-9}$ g/ml. This solution contained barium as a carrier. The concentration of barium nitrate in this solution was equal to 0.1 g/ml.

For subsequent measurements of the emanation (Rn) it proved sufficient to introduce $6\text{-}7 \cdot 10^{-9}$ g Ra per 1g of precipitated hydroxide or carbonate.

The technique of measuring the evolved emanation and the preparatory operations were taken from the works of I. E. Starik and his collaborators [5]. The amount of emanation was measured with a SG-1M electrometer.

As special experiments have shown, the topochemical processes which have been studied by us can be interrupted at any moment with a subsequent return to the same point on the kinetic curve. For this reason measurements of the emanation coefficients of specimens of the carbonates and hydroxides at various stages of transformation were performed after this process had been halted by quenching. The accumulation of the radon, and the measurements with the electrometer, were carried out at room temperature.

The hydroxides of magnesium and zinc were obtained by precipitation at 40° from concentrated nitrate solutions, using a concentrated sodium hydroxide solution. The precipitation was performed during continuous mixing. After precipitation, the hydroxides of magnesium and zinc were carefully washed free of contaminating electrolytes by repeated decantation. Magnesium carbonate was obtained by precipitation at room temperature from a concentrated solution of magnesium nitrate, using a concentrated sodium carbonate solution which was saturated with carbon dioxide. The basic carbonate which was obtained was calcined to a constant weight in a current of dry carbon dioxide gas at a temperature of 150°. The content of carbon dioxide in the material prepared in this way corresponded to that of the normal carbonate.

Zinc carbonate was prepared by precipitation, through mixing a concentrated solution of zinc nitrate, cooled to 5°, with a concentrated sodium bicarbonate solution which had been previously saturated with carbon dioxide. In each case, prior to precipitation, there was added to the solutions of the nitrates of magnesium and zinc the above mentioned solution of radium nitrate with its accompanying barium nitrate.

TABLE 1

Values of the Emanation Coefficient for the Transformation of Hydroxides and Carbonates to Oxides

Compound	K_{eman}, %	Temperature of calcination, °C	Duration of calcination, hours
Magnesium hydroxide →	2-3		
magnesium oxide	10-12	550	2
Basic magnesium carbonate →	8-9		
normal magnesium carbonate	1-2	150	4
Normal magnesium carbonate →	1-2	450	2
magnesium oxide	2-5		
Zinc hydroxide →	20-25		
zinc oxide	2-3	550	2
Normal zinc carbonate →	80-85		
zinc oxide	4-5	450	2

As it turned out, the hydroxides of magnesium and zinc took up about 50% of the radium which was introduced, but more than 90% of this amount was removed by washing the precipitates, the takeup of radium thus falling to 2-5 weight % of the initial material. In this respect the carbonates differ favorably from the hydroxides, since they, taking up this same 50-60% of the introduced radium, fully retained the same during washing. The result is that the takeup of radium by the carbonates is approximately 10-20 times greater than by the hydroxides for the same amount of radium introduced. With such coefficients for the takeup, and taking into account differences in the atomic weights of barium and magnesium, the content of $Ba(OH)_2$ in the hydroxide of magnesium amounted to less than 0.4 at.% and the content of $BaCO_3$ in magnesium carbonate, to 4-8 at.%. Decomposition of the carbonates and the hydroxides was brought about in a vacuum system at a pressure of $5 \cdot 10^{-2}$ mm. Prior to decomposition, the specimens were treated for the removal of hydroscopic moisture. The extent of transformation was determined by weighing the specimens. For a number of specimens the specific surface was determined according to the BET method by measuring the absorption of n-heptane vapors. By studying the relation between the emanation coefficient and the calcination temperature of magnesium hydroxide, it was established, just as in the work of Friske and Feichtner [6], that the maximum change in this coefficient occurs at a temperature of 400°.

In Table 1 there are shown values of the emanation coefficient as observed for transformations from the hydroxides and the carbonates to the corresponding oxides by calcination. From these data it can be concluded that the emanation coefficient is considerably changed as the result of these transformations.

The magnitude of the emanating power also depends on the calcination temperature. For magnesium we have determined the change in the emanating power in the sequence of transformations: magnesium hydroxide-basic carbonic-normal carbonate-magnesium oxide. The emanation coefficient is at a maximum for the basic carbonate and falls on transition to the normal carbonate, this possibly being the result of the diminution of the specific surface of the latter from 25 m^2/g to 10 m^2/g. For zinc the corresponding sequence did not involve the basic carbonate. The emanating powers of the hydroxide and the carbonate of zinc diminish on transition to the metallic oxide. The data presented in Table 1 point to the considerable influence of the topochemical processes on the emanating powers of the systems studied. The continuous change in the emanation coefficient during the topochemical processes of disintegration of the carbonates and the hydroxides might give a characteristic of the fine structural transformations which are completed in the various stages of this process. Measurement of the specific surfaces of a series of specimens of hydroxides and carbonates at various stages of the transformation make it possible to take into account the influence of the magnitude of the surface on the emanating power.

The dependence of the emanating power, and the specific surface, on the percent transformation of the carbonates and the hydroxides of magnesium and zinc is graphically represented in Figs. 1-2.

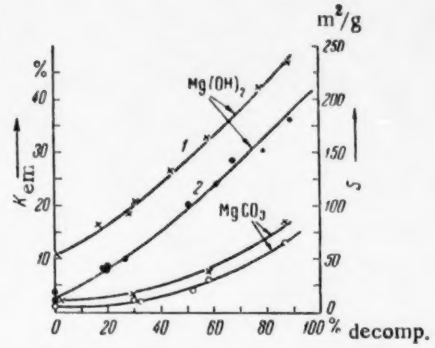

Fig. 1. The dependence of the emanation coefficient (2, 4) and the specific surface (1, 3) on the extent of transformation of magnesium hydroxide and magnesium carbonate.

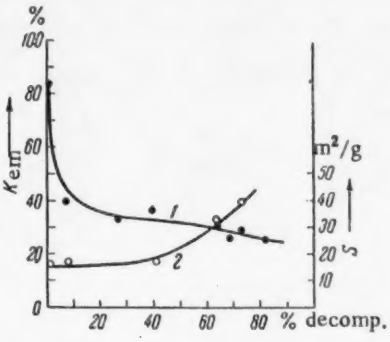

Fig. 2. The dependence of the emanation coefficient (1) and the specific surface (2) on the extent of decomposition of zinc carbonate.

It follows from Fig. 1 that during the dehydration of magnesium hydroxide at 320° the emanation coefficient increases with increasing percentage transformation. At the same time there is also to be observed an increase in the specific surface. The curves showing the dependence of the emanation coefficient, and the specific surface, on the percentage transformation are similar. At the end of the process of dehydration (92% transformation) the emanation coefficient has changed 20-fold and has the magnitude of the specific surface, 5-fold.

For magnesium carbonate the dependence of the emanating power and the specific surface area (Fig. 1, 3 and 4) on the percentage decomposition at T = 370° have similar character. In this case also, there is a sharp increase in the emanation coefficient, amounting to 9.3-fold at 80% decomposition of the carbonate. The specific surface is at the same time increased by 8.5-fold.

A different picture is to be observed during the decomposition of zinc carbonate and the dehydration of zinc hydroxide. It follows from Figure 2, that during the decomposition of zinc carbonate the emanating power decreases as the extent of transformation rises, there being a simultaneous increase in the magnitude in the specific surface. Thus in this case, the course of the curves characterizing the relation of the emanation coefficient, and the specific surface, to the extent of transformation in the topochemical process are opposite to one another. A similar, but weaker, dependence is also observed for zinc hydroxide. In Fig. 3 there is graphically represented the relation between the emanating power, and the specific surface, during the topochemical process in the three systems which we have studied. From this diagram it follows that the dependence of the emanation coefficient on the specific surface in the process of dehydrating magnesium hydroxide is linear in character. The dependence of the emanation coefficient on the magnitude of the specific surface in the decomposition of magnesium carbonate is similar.

The results of the measurements which have been carried out on the change in the emanating power and the magnitude of the specific surface, indicate the existence of essential alterations in the structures of the hydroxides and carbonates of zinc and magnesium during the topochemical processes of their disintegration.

The similar courses of the curves characterizing the relation between the emanation coefficient, and the magnitude of the specific surface, and the extent of transformation in the decomposition processes in magnesium hydroxide and carbonate, as well as the linear dependence of the emanation coefficient on the magnitude of the specific surface, show that the alteration of the specific surface is the basic factor determining the emanation coefficient during the studied topochemical processes.

The linear relation between the change in the emanation coefficient and the magnitude of the specific surface in the course of the topochemical process indicate, in all likelihood, the formation of solid solutions of the carbonates of magnesium, barium and radium which result from precipitation. This supposition is also supported by data on the similarity of the crystallochemical structures of the carbonates of magnesium and barium [7] and, probably, of radium. As to the hydroxides of magnesium, barium and radium, it is possible, in view of the small content of the latter, that even in this case solid solutions are formed or there is a microheterogeneous distribution between the grains of the magnesium hydroxide. In the case of the carbonate and the hydroxide of zinc it is clear that there is a different type of takeup of the radium. Taking into account the very high emanation coefficients of the initial compounds, it is possible to postulate an absorptional character for the takeup of radium, which in the form of a carbonate or hydroxide, deposits on the surface of the initial solid phase during precipitation.

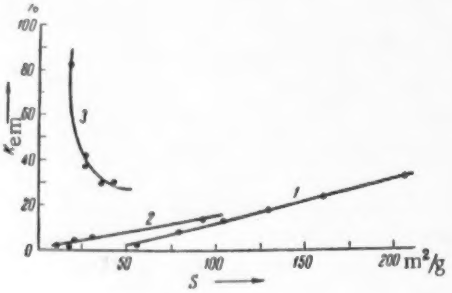

Fig. 3. The dependence of the emanating ability on the magnitude of the specific surface at fixed degree of transformation in magnesium carbonate (2) and hydroxide (1), and in zinc carbonate (3).

The diminution of the emanation coefficient with increasing specific surface during the topochemical disintegration of the compounds of zinc could possibly be explained as the effect penetration of radium into the interior of the solid phase, which would hinder the evolution of radon. For radium, similar phenomena have been observed by Otto Hahn [2] during the heating of barium nitrate and lead nitrate. Thus this unusual relationship of decreased emanating power with increased specific surface, could, in this instance, be the result of the secondary effect of a diffusion of radium into newly formed zinc oxide or the envelopment of the zinc oxide by compounds of radium and barium. It appears to us that further applications of the emanation method to the study of the topochemical steps in the preparation of catalysts could disclose a whole series of new relationships. In this connection interest attaches to the new method which has been developed by Iech [8].

The authors count it their pleasant duty to express their thanks to I. E. Starik, Corresponding Member of the Academy of Sciences of the USSR and to O. S. Melikova for consultation and for aid in matters of technique.

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AN INVESTIGATION OF CHEMICAL ADSORPTION ON SOLID SOLUTIONS OF NICKELOUS OXIDE

N. P. Keier and L. N. Kutseva

(Presented by Academician P. A. Rebinder May 13, 1957)

The electrical conductivity of nickelous oxide can be varied over wide limits by dissolving in its lattice oxides of metals which differ from nickel in their valence [1]. For the development of a theory of chemical adsorption on semi-conductors special interest attaches to the study of adsorption in systems which differ from one another in electronic properties. We have investigated the chemical adsorption of oxygen, which takes place with electron capture, and the adsorption of the gases CO and C_2H_2, which occurs with loss of electrons. As special measurements have shown, the adsorption of these gases is accompanied by oppositely directed changes in the electrical conductivity. In the first case the conductivity is increased; in the second it is diminished.

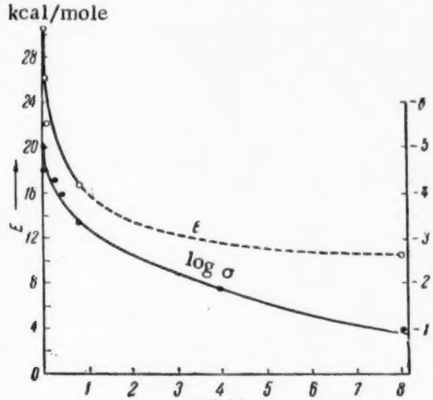

Fig. 1. The dependence of the electrical conductivity of solid solutions of NiO with Li_2O, and the energy of activation for electrical conductivity, on the concentration of the Li^+ cation in the NiO lattice.

Nickelous oxide was prepared by the decomposition of nickel carbonate in air at 900° in the course of 2.5 hours. Solid solutions were obtained under these same conditions by the decomposition of nickel and lithium carbonates mixed in definite proportions.

With increasing concentration of the lithium cation in the lattice, the parameters of the latter are decreased. In Fig. 1 there is shown the change in the electrical conductivity, and the energy of activation for conduction, in their dependence on the concentration of the lithium cation in the nickelous oxide lattice. The electrical conductivity was measured in air at room temperature.

Adsorption was studied in a vacuum system by measuring the pressure drop as recorded on a McLeod guage. In order to exclude the influence of pressure on the kinetics, the pressure drop was limited to 10% of the initial value and the pressure was then once more brought back to the initial value by the introduction of gas from a large sphere at constant pressure. The catalyst was protected from oil and mercury vapors by two U-shaped traps, one of which was inserted in a quartz reactor [2].

The Adsorption of Oxygen

NiO, NiO-Li_2O solid solutions containing 0.8 and 8.0% lithium cations, as calculated on the basis of the total number of cations, and NiO-Fe_2O_3 (1 at.% Fe) were investigated. Adsorption was studied over the temperature interval 200-360°. Below 200° the rate of adsorption is low. In Fig. 2 there are sketched kinetic isotherms for the adsorption of oxygen on 1 m^2 of surface. It can be seen that the rate of adsorption is increased by dissolving lithium oxide in the nickelous oxide. The energies of activation, calculated according to the Arrhenius Law from ratios of adsorption rates at uniform coverage, are presented in Table 1. Increasing the lithium ion content from 0.8 to 8% is without influence on the adsorption.

The calculated values point to a diminution of the activation energy for the oxygen adsorption as a result of the dissolving of lithium oxide, and to an increase in the energy of the activation for this adsorption with a rise in the degree of coverage of the surface.

$$q = At^{1/n}, \tag{1}$$

For nickelous oxide the kinetic isotherm satisfies an equation in which 1/n varies directly with the temperature. On a solid solution of nickel and lithium oxides there is a change in the kinetic law for the oxygen adsorption. In this case the law is of the form:

$$q = A' \ln t. \tag{2}$$

This is a rare case in which the equation is fulfilled for investigations of adsorption over a wide range of times at constant pressure. The dissolving of Fe_2O_3 decreases the rate of oxygen adsorption and raises the activation energy of the adsorption.

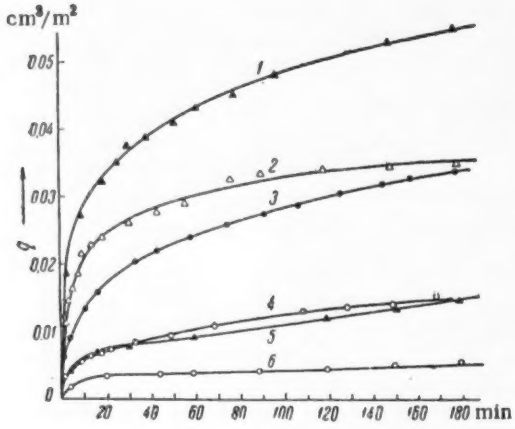

Fig. 2. Kinetic isotherms for the adsorption of oxygen, P_0 = 0.44 mm of Hg. 1) T = 360°, NiO + + 8 at.% Li; 2) T = 360°, NiO; 3) T = 310°, NiO + 8 at.% Li; 4) T = 310°, NiO; 5) T = 210°, NiO + 8 at.% Li; 6) T = 210°, NiO.

TABLE 1

Values of the Activation Energy for the Adsorption of Oxygen, Calculated from the Arrhenius Equation (kcal/mole)

Coverage, cm³/m²	NiO	NiO(Li_2O)
0.005	30.0	–
0.010	40.0	–
0.020	–	18.0
0.030	–	24.0

The Adsorption of Carbon Monoxide

The adsorption of CO takes place with appreciable velocity even at room temperature. The adsorption rate rapidly diminishes with an increase in the coverage; the maximum coverage of the surface is not great; at room temperature and after 3 hours there is adsorbed a volume of CO corresponding to 5.0% of a monomolecular layer, as calculated on the supposition that each Ni^{2+} cation is capable of adsorbing a single molecule of CO. In addition to the adsorbed gas, 10% of the CO which is taken up is oxidized to CO_2 at the expense of the oxygen of the NiO. At 102° after 3 hours there is adsorbed a volume of CO which corresponds to a 5.0% surface coverage and the oxidized CO amounts to 25% of that which has been taken up.

Dissolving Li_2O in nickelous oxide diminishes the rate of adsorption of CO and the degree of surface coverage (Fig. 3). With 0.4 at.% dissolved Li, the adsorption in the first minute corresponds to 0.7% of a monolayer and remains unchanged up to 280°. By dissolving Fe_2O_3 in NiO in an amount corresponding to a concentration of 1 at.% Fe, the rate of adsorption of CO is diminished (Fig. 3, 4). On introducing 1.2 at.% Fe from $Fe(NO_3)_3$ into a sample of NiO containing 0.8 at.% Li, there is observed a partial reestablishment of the ability of the latter to adsorb CO (Fig. 3, 5).

The Adsorption of Acetylene

In distinction to CO, a high surface coverage is reached in the adsorption of C_2H_2 over a period of 3 hours: at 20°, 22%; at 79°, 53% and at 116°, 68%.

Despite a considerably higher degree of surface coverage as compared with CO, similar small amounts of dissolved lithium oxide also exert a retarding influence on the adsorption of acetylene (Fig. 4). The dissolving of 0.4 at.% lithium almost completely surpresses the adsorption of acetylene up to 300°. Above 300°, measurements of adsorption are without meaning since in in this region of temperature there are observed secondary processes of oxidation and decomposition of the C_2H_2.

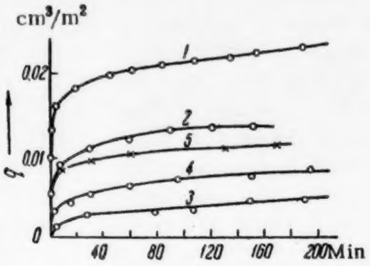

Fig. 3. Kinetic isotherms for the adsorption of carbon monoxide. 1) T = 20°, P_0 = 0.096 mm of Hg, NiO; 2) T = 20°, P_0 = 0.094 mm of Hg, NiO + 0.1 at.% Li; 3) T = 20°, P_0 = 0.088 mm of Hg, NiO + + 0.2 at.% Li; 4) T = 20°, P_0 = 0.092 mm of Hg, NiO + 0.82 at.% Li + 1.23 at.% Fe; 5) T = 20°, P_0 = 0.09 mm of Hg, NiO + 1 at.% Fe.

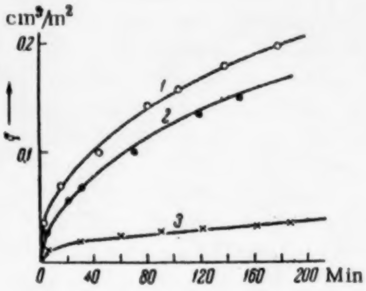

Fig. 4. Kinetic curves for the adsorption of acetylene. 1) T = 80°, NiO; 2) T = 80°, NiO + 0.1 at.% Li; 3) T = 125°, NiO + 0.2 at. % Li.

By the introduction of 0.2 at.% Li, the rate of adsorption is decreased to such an extent that it practically ceases at room temperature, and at 125° and after 3 hours totals only 13.5% of a monolayer.

The introduction of 0.1% Li slightly diminishes the rate of adsorption at low coverage. The extent of coverage is thereby changed but very little. Values of the energy of activation for adsorption, calculated from the Arrhenius equation at uniform surface coverage, using the temperature dependence of the adsorption rate, indicate that this energy is increased by the dissolving of lithium oxide.

The Adsorption of CO_2

The adsorption of carbon dioxide on nickelous oxide is small; it amounts on NiO at 26° to a 2.4% coverage of the surface, and on a solid solution of NiO with lithium oxide containing 8 at.% Li, to 3.5%. The kinetic isotherm for the adsorption on nickelous oxide satisfies Equation (1).

DISCUSSION OF RESULTS

This study has shown that the dissolving of lithium oxide in NiO lowers the rate of adsorption of CO and acetylene and increases the rate of adsorption of oxygen and CO_2. In the first group there are included those gases which are electron donors, the adsorption of these being accompanied by electron transfer from the adsorbing molecules to the catalyst; in the second there are the electron adsorbers which extract electrons from the catalyst according to the reactions:

$$(1)\qquad CO + Ni^{3+} \rightarrow (CO)^{+} Ni^{2+},$$

$$(2)\qquad \frac{1}{2}\,O_2 + 2Ni^{2+} \left\langle \begin{array}{l} O^{2-}(Ni^{3+}) + Ni^{3+} \\ O^{-}(Ni^{3+}) + Ni^{2+}. \end{array} \right.$$

NiO is a perforated semi-conductor in which the passage of current is realized by means of transfer of electrons between the Ni^{3+} and Ni^{2+} which are located at the lattice points. Each Ni^{2+} cation on the surface, as a result of an interchange with an Ni^{3+} from the bulk, passes after a finite time over into a Ni^{3+} cation, this time being the greater, the nearer the lattice point is to an Li^+ cation. The concentration of the Ni^{3+} and the electrical conductivity can be raised by dissolving into the NiO lattice, oxides of univalent metals (in our case Li_2O) or superstoichiometric oxygen [3]; in both cases there results a black nickelous oxide. It has been shown that the increase in concentration of Ni^{3+} in NiO which results from the dissolving superstoicheometric oxygen only slightly diminishes the adsorption of CO and C_2H_2 on unit surface, although in terms of its electrical conductivity, the specimen corresponded to a nickel oxide containing 0.9 at.% Li. This fact leads to the supposition that the retardation in the adsorption of CO and C_2H_2 which results from dissolving Li_2O in NiO is connected with the presence of the Li^+ cations on the surface. This hypothesis eliminates the contradiction between an increase in the concentration of the Ni^{3+} cations, which are adsorption centers for CO and C_2H_2, and a decrease in the rate of adsorption of these gases as a result of dissolving Li_2O in NiO. The influence of the Li^+ cations on the neighboring Ni^{2+} cations is related to the fact that in the lattice points in which they are found, the charges of the neighboring oxygen ions are not compensated. Cations with anomalous charges form strong electrostatic fields which alter the work of electron extraction from the neighboring cations in the lattice. The transition of Ni^{2+} into Ni^{3+} at points which are neighboring to Li^+ must be thereby rendered easier, this leading to a diminution of the energy of activation for the adsorption of oxygen on the Ni^{2+} cations which are near to Li^+. An inverse influence would be exerted by the Li^+ cations on the reactivity of the Ni^{3+} cations which are located on neighboring lattice points. As a result of the interaction between them, their reactivity according to Reaction (1) is diminished. It follows from the experimental data, that a Li^+ cation acts over several of the nearest cation lattice points. The further the lattice points are removed from the Li^+ cations, the easier is the adsorption of CO and C_2H_2 on the Ni^{3+} cations.

That nonuniformity in the active surface of nickelous oxide which was established by the isotope method [4], finds here its explanation.

The diminution of the rate of adsorption of CO which results from the dissolving Fe_2O_3 is related to the decrease in the concentration of the Ni^{3+} cations. On dissolving Fe_2O_3 in NiO containing Li_2O, the cations Fe^{3+} distribute themselves in lattice points which are neighbors to the Li^+ and screen the action of the latter. With a cation ratio $Li^+ : Fe^{3+}$ of 1:1 the adsorbability is not reestablished. An excess of the Fe^{3+} cations of about 1:1.2 is required in order that there be a partial return to the adsorbability shown by NiO containing 0.8 at.% Li.

There is a complete similarity between the influence of dissolved iron and lithium oxides on the chemical adsorption of carbon monoxide by NiO and the catalytic oxidation of carbon monoxide which has been studied earlier [5]. We have made an attempt to explain the complex interrelations resulting from the investigation of the catalytic and chemosorptive properties of solid solutions of NiO which differ from one another in their electronic structures. It is completely conceivable that there are also other possible explanations of these results. Further investigations will help in a definitive interpretation of the results of investigations of solid solutions of oxides differing in their electronic structures, such as is needed for the construction of a theory of surface activity and catalysis in semi-conductors.

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THE ENTHALPY OF POLYMERIZATION OF THE CYCLIC FORMALS

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(Presented by Academician A. A. Balandin May 25, 1957)

The polymerization of heterocyclic compounds is of undoubted interest, both from the theoretical and from the practical points of view. Many instances are known of pronounced differences in the general reactivity of the heterocyclic compounds in a single homologous series and, in particular, in the ability of such compounds to undergo polymerization, this ability depending on the number of members in the cycle. Under the same reaction conditions, the 5- and 6-membered cycles of each series usually prove to be considerably less reactive than are the 7- and 8-membered cycles of the same series, cycles with a greater number of members having scarcely been investigated.

Since both the attacking agent and the attacked heterobond are the same in analogous reactions of the various heterocycles of a given series, the cause of the pronounced differences in the reactivities of the separate representatives of the series should be sought in thermodynamics.

The attempt, made by one of us [1], at a general thermodynamic study of the polymerization reactions of heterocyclic compounds could not go beyond the establishment of certain general propositions, the development of these latter demanding a great amount of experimental material which is not available at this time.

Recently the question of the free energy changes in the polymerization reactions of cyclic compounds has been carefully considered by Dainton and his collaborators [2]. Making use of trustworthy experimental data and supplying values which were lacking by extrapolation with the aid of semiempirical equations, these authors calculated values of ΔH, ΔS and ΔF for the cyclanes (up to, and including, cyclooctane) and for polymethylene. By comparing the values obtained in these calculations, it was easy to evaluate the changes occurring in these functions in a hypothetical polymerization reaction, cyclane (liq)—polymethylene(liq), at standard temperature.

The values of the standard entropies of cycloheptane and cyclooctane which were obtained in [2] by extrapolation differ up to 9 cal/mole · deg, however, from those experimentally determined by Finke and his collaborators [3].

Even less trustworthy results follow from an attempt to extend to even the simplest series of heterocyclic compounds the conclusions obtained for the cyclanes [4]. In this field there is an almost complete lack of experimental material and the accumulation of such data is vitally necessary.

In a series of our papers we have set ourselves the task of obtaining experimental material on the change of enthalpy in the polymerization of various series of heterocyclic compounds, principally those with from 5 to 8 members in the cycle. The total absence of data on the entropy of these compounds, and of the linear polymers corresponding to them, makes it impossible to calculate values for ΔF in the polymerization reactions. We presume, however, that even information concerning the changes in enthalpy in these processes would undoubtedly prove to be useful for the explanation of differences in the reactivity of the heterocyclic compounds of a given series.

In one of our papers [5] we have shown that for a number of lactams (with from 5 to 8 members in the cycle) the enthalpy of ring formation i.e., the change of enthalpy in the polymerization reaction, can qualitatively explain the differences in reactivities in regard to this reaction.

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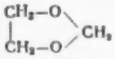
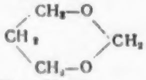
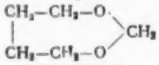
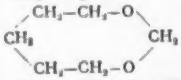
* Deceased.

After a detailed investigation of the equilibria in the polymerization reactions of the cyclic formals (with from 5 to 8 members in the cycle) [6], it seemed of undoubted interest to investigate the heats of combustion of these compounds and from a comparison of the experimentally determined heats of combustion, calculated for a given compound in terms of increments due to the atomic groups entering into it, to determine the magnitude of the enthalpy of ring formation (as has been done for the lactams in [5]). The means for carrying on such a calculation and its validity have been considered in [5].

It was, in addition, of interest to compare the values of the enthalpy of ring formation in the formal series with the corresponding values for the cyclanes, trustworthy data on the combustion of these latter, referred to the gaseous state, being found in the literature [7, 8] (in the case of the lactams, [5], such a comparison could not be made because of the lack of acceptable data on the heats of fusion and sublimation).

The technique which was employed for the determination of the heats of combustion, and which was described by us earlier [9], made it possible to obtain results which are accurate to 0.02-0.03%. All of the materials which have been investigated in this work are liquids at room temperature; they were burned in a bomb calorimeter in fused thin-walled glass ampules. The physical constants of the investigated materials and the experimental data obtained by us are presented in Table 1.

TABLE 1

Compound	Formula	B.p. °C	n_D^{20}	d_4^{20}	$-\Delta H_c^{20}$, kcal/mole (liq)	Heat of vaporization, kcal/mole	ΔH_c^{20}, kcal/mole (gas)
Ethylene-formal		76.0	1.4002	1.0595	407.6	8.3	415.9
Trimethylene-formal		103.5—104	1.4183	1.0319	557.4	9.4	566.8
Tetramethyl-eneformal		117—117.5	1.4307	1.0023	719.4	9.8	729.2
Pentamethyl-eneformal		134	1.4383	0.9886	884.0	10.7	894.7
Dibutylformal	$C_4H_9-O-CH_2-O-C_4H_9$	180	1.4060	0.8340	1398.7	13.7	1412.4

The quantities ΔH_C^{20} represent the change in enthalpy expressed in $kcal_{15°}$, for the isothermal (20°) combustion of the test materials in the liquid state under a pressure of 1 at. and with the formation of gaseous CO_2 and liquid H_2O as combustion products.

The heats of vaporization of the investigated materials at 20° which are presented in Table 1 have been calculated by us to an accuracy of 1-2%, using semiempirical relations [10].

In the last column there are shown heats of combustion at 20°, referred to the substances in the gaseous state.

From the data which have been obtained, values for the enthalpy of ring formation were calculated as differences between the heats of combustion of the respective compounds in the gaseous state and the heats of combustion calculated additively for these compounds in terms of increments due to the various groups. For the increment in the heat of combustion per $-HC_2-$ group there was taken a value of 157.4 kcal, which is known for the alkanes from the literature [11]. The increment in the heat of combustion per $-O-CH_2-O-$ group was determined by comparing the heat of combustion found by us for dibutylformal with the heat of combustion of normal octane [11]; it proved to be equal to 94.9 kcal.

In Table 2 are presented enthalpies of ring formation for cyclic hydrocarbons [7, 8] and for the formals.

TABLE 2

Enthalpies of Ring Formation for Hydrocarbons and Formals (kcal/mole)

Number of members in the cycle	Hydrocarbon	Formal
5	6.6	6.2
6	0.1	0.0
7	6.2	4.7
8	9.6	12.8

It is to be seen from Table 2, that for both series of compounds, the minimum value of the enthalpy of ring formation is associated with the 6-membered cycle and the maximum, with the 8-membered cycle.

The values of the enthalpies of ring formation for alkanes and formals containing the same number of members (with the exception of the 8-membered compounds) are close to one another. It should be noted that the excess enthalpy of the cyclic formals decreases in the sequence $8 > 5 > 7 > 6$, just as is the case with the alkanes. Quantitative investigations of the polymer $\rightleftharpoons$ monomer equilibra for the cyclic formals [6] has shown that the tendency of these latter to polymerize depends on the number of members in the ring and diminishes in the sequence $8 > 7 > 5 > 6$, the 5- and 7- membered cycles differing but little in their ability to polymerize.

Comparing these data with the values of the enthalpy of ring formation which have been obtained in the present work, it can be concluded that this last quantity permits an evaluation of the relative polymerization abilities of the compounds of a given series.

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THE DEPARTURES OF THE THERMODYNAMIC PROPERTIES OF SOLUTIONS OF STRONG ELECTROLYTES FROM THE LIMITING LAW IN THE DEBYE REGION OF CONCENTRATIONS

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(Presented by Academician I. I. Chernyaev April 27, 1957)

In the Debye-Hückel theory [1] the solvent is considered as a continuous medium characterized by a macroscopic dielectric constant, D_0, which is independent of the distance from the ion center and the concentration of the electrolyte; in the calculation of the free energy of the solution no account is taken of the contribution arising from the presence of ion pairs nor of the dependence of the free energy of solvation on the concentration. Up to the present time it has been insufficiently clear as to how far these effects should be taken into account in the Debye region of concentrations [2] in order to explain the deviations from the limiting law. It is clear that their role will be reflected in a varying degree in the several properties of the solution. Those nonelectrostatic terms in the free energy of the solution which arise from the formation of ion pairs (ΔG_c) and from the alteration in the structure of the solution (ΔG_p), can be small in comparison with the electrostatic contribution to the free energy, ΔG_D, which is fixed by the first order approximation equation of Debye-Hückel [1], whereas their temperature derivatives, speaking generally, can be close to one another in order of magnitude. Thus in the case of the heats of dilution, considerable divergence might be expected between the experimental and the theoretical values, ΔW and ΔW_D, especially at temperatures close to the t_{mp} of the solvent, when the structure of the latter is disturbed but little by the thermal motion.

Concerning the heats of dilution of nonaqueous solutions of strong electrolytes in the Debye region, or on its boundary, data is to be found in the literature only for NaCl in ethylene glycol at 25° [4] ($D_0 = 37.7$) and for HCl in H_2O-dioxane mixtures of various compositions at 0-50° [5] ($D_0 = 10$-80); for the mean heat of dilution, $\Delta W_{c_1}^{c_2}$, there is data on NaCl, NaBr and NaI solutions in formamide at 25° [6] ($D_0 = 109$). In the first two cases the observed deviations between ΔW and ΔW_D are of the same order as for aqueous solutions. In the case of formamide, $\Delta W_{c_1}^{c_2}$ is, in distinction to the aqueous solutions of the same concentration, of opposite sign to the theoretical value.

We have measured the integral heats of solution, ΔH_m, of NaCl, KCl, RbCl and CsCl in H_2O_2 at 0° ($D_0 = 84.2$; $t_{mp} = -0.49°$ [3]) at $c = 0.004$ moles/liter and up. These measurements were carried out in an ice calorimeter. The accuracy of the determination of ΔW from ΔH_m amounted to ± 7-15% in the case of the solutions of NaCl in 99.99% H_2O_2 and to ± 10-30% in all of the remaining cases. From the graphs of Figure 1 it is to be seen that in H_2O_2 a difference of sign between ΔW and ΔW_D is first noted at much lower concentrations than is the case in H_2O.

Calculations for $D = f(c)$, for multiple collisions, the natural volume of the ions, the variation of the distance of closest ion approach, a, with temperature, etc., are not adequate to explain the existence of positive heats of dilution in the Debye region of concentrations. The only conceivable causes for this effect are the formation of ion pairs and the change in structure of the solution with concentration.

In its most general form, the calculation for ΔG_c can be made on the basis of the Bronsted-Guggenheim theory of the "specific interaction" of ions [7, 8].

Guggenheim [8] supposes in fact that $U_c(r_{ij}) = u_k(r_{ij})$, where $u_k(r_{ij})$ is the potential energy of quantum mechanical interaction. The actual picture is more complex. We will consider the specific interaction of ions resulting from their approach to a distance $r_{ij} < a_i + a_j$ (a_i and a_j being the radii of the solvation spheres of the ions). Then for any ion pair

$$U_c(r_{ij}) = \begin{cases} 0 & \text{where } r_{ij} \geqslant a_i + a_j \\ U_c(r_{ij}) & \text{where } a \leqslant r_{ij} < a_i + a_j \\ +\infty & \text{where } r_{ij} < a \end{cases} \tag{1}$$

For $a < r_{ij} < a_i + a_j$ the inequalities $1 < D(r) < D_0$ and $u_k(r_{ij}) < 0$ are valid. If $r_{ij} = a + 4r_p$ (r_p being the radius of the solvent molecule) it is then possible to consider that [9] $D(r) \approx n^2 \approx 3-4$, where n is the refractive index.

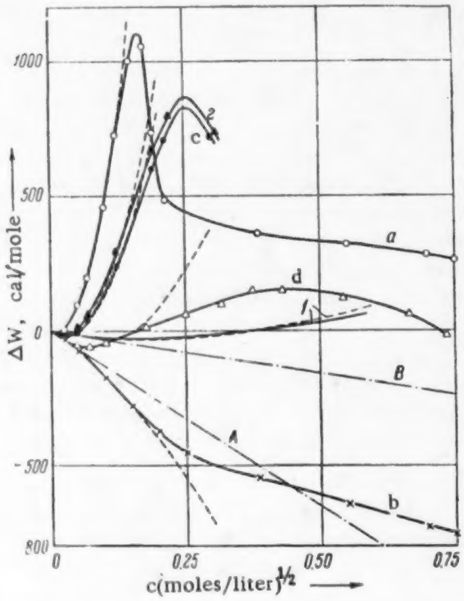

Fig. 1. Integral heats of dilution at 0°. A) limiting law, H_2O_2; B) limiting law, H_2O. 1) KCl in H_2O (recalculated by us to 0° from the data of [11] at 12.5°); H_2O_2, 99.99%: a) NaCl, b) KCl, c) RbCl, d) CsCl. H_2O_2, 94.29%: 2) KCl. The full curves represent experimental data; the dotted curves, theoretical values according to Equation (6).

This gives

$$-[u_e(r_{ij}) + u_k(r_{ij})] \gg kT, \tag{2}$$

$$\text{where } u_e(r_{ij}) = \frac{e_i e_j}{r_{ij} D(r)},$$

and e_i and e_j are the ionic charges. According to (2), there should be a strong association, which, in the case of strong electrolytes, is not observed in practice. This can be explained by the fact that a partial desolvation of the ions occurs during the formation of an ion pair. The difference between the potential energies of solvation of the ion pair and of the free ions, $\Delta u_c(r_{ij})$, plays the role of an effective energy of ion repulsion, so that, finally *

$$U_c(r_{ij}) = u_e(r_{ij}) + \Delta u_c(r_{ij}) + \\ + u_k(r_{ij}) \tag{3}$$

and

$$|U_c(r_{ij})| < kT. \tag{4}$$

In the Debye-Hückel theory, the relation (4) was obtained by an artificial procedure wherein it was considered that $D(r) = D_0$ for all r_{ij}, this being in contradiction to the actual physical picture of the effect. Thus the introduction into (3) of an expression of the type $\Delta u_c(r_{ij})$, to describe the short range forces of repulsion (which are however "long range" in comparison with those corresponding to the term $u_k(r_{ij})$ is physically indispensable.

Since the potential energy of solvation depends on the solution structure, and since the latter varies with the concentration, $U_c(r_{ij})$ must depend on the concentration through $\Delta u_0(r_{ij})$. But $\Delta u_c(r_{ij})$ is a different term; to a first approximation, it can be considered that the change in the structure of the solution is reflected to the

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* With such a model, the requirement that $U_c(r_{ij}) = 0$ when $r_{ij} \geq a_i + a_j$ is purely formal. It is needed in order to fulfill the condition $\Delta G_c = 0$ when $r_{ij} \geq a_i + a_j$. This can be achieved by other means as well, but, since the calculation of the integral in (1) is not carried out in what follows, the choice of path is of little significance.

same extent in the potential energy of solvation of the ion pair and the free ions, and to thus suppose that $\Delta u_c(r_{ij})$ does not depend on the concentration. This assumption is the more exact, the lower the concentration.

To the same degree of approximation, it can be considered that in the Debye region of concentrations, ΔG_p makes a contribution to ΔW which is of the type $\Delta W_p = K_2 c$.

It is not possible at the present time to find a clear-cut expression for $U_c(r_{ij})$. We will set

$$\beta = \int \left(e^{-\frac{U_c(r_{ij})}{kT}} - 1\right) d\omega \text{ and } \varphi = \frac{1}{V}\frac{\partial V}{\partial T}\,. \tag{5}$$

Making use of the usual thermodynamic relations and taking ΔW_p into account, we obtain,

$$\Delta W = \Delta W_D + K_1 c + K_2 c = \Delta W_D + Kc, \tag{6}$$

where

$$K_1 = RT^2 N \cdot 10^{-3}\left(\varphi \cdot \beta - \frac{\partial \beta}{\partial T}\right) \tag{7}$$

(N is Avogadro's Number).

It is to be seen from Figure 1 that the agreement between calculation and experiment is satisfactory up to $c = 0.025$, i.e., up to the limit of the Debye region. For comparison, corresponding calculations have been carried out on the data of the literature for NaCl in ethyleneglycol at 25° [4], for NaCl, NaBr and NaI in formamide at 25° [6], for NaCl in H_2O at 25 and at 10° [10] and for KCl in H_2O at 25, 12.5 and 0° [11]. The curve of ΔW for KCl in H_2O at 0° is plotted as being typical for the aqueous solutions of the investigated group of salts, NaCl-CsCl. It was found that the range of concentrations for which agreement between calculated and experimental values of ΔW is observed extends furthest ($c > 0.1$) for aqueous solutions and is least extensive for solutions in hydrogen peroxide; also, at a given concentration, the discrepancy between experimental and calculated values of ΔW is greatest for hydrogen peroxide and least for water. Ethylene glycol and formamide occupy intermediate positions.

According to Equations (3) and (4), $U_c(r_{ij})$ is a small difference of large quantities and, accordingly, small variations in $\Delta u_c(r_{ij})$, resulting from alterations in the structure of the solution, can bring about considerable change in K_1; at the same time there can also be an alteration in K_2. Consequently, the most pronounced deviation between the calculated and the experimental ΔW's should be expected in those cases where the structure of the solution most strongly varies with the concentration.

TABLE 1

Solvent	t° C	$-\beta \cdot 10^9$	$\varphi \cdot 10^4$	Source
Water	0	4.56	—0.7	([19], [21])
	25	4.54	2.57	([19], [20])
Ethylene-glycol	25	5.16	6.48	([22])
Formamide	25	6.54	7.41	([6])
H_2O_2	0	7.55	8.41*	([3])

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* Over the interval 0-10°.

Starting from the available information and concepts concerning the structures of H_2O [12] and dilute aqueous salt solutions [13-15], it can be considered that, in the case of small spherical ions, the alteration with concentration of the structures of aqueous solutions will be small, at least up to $c = 0.1$. According to the x-ray data of Randall [16], H_2O_2 is a liquid showing dense molecular packing. It is reasonable to expect that one and the same kind of ion would disturb the structure of a dense-packed liquid with nonspherical molecules (H_2O_2) to a greater extent than would be the case with water. It is known further that, to a certain degree, the disturbing action of ions on a liquid structure is similar to a thermal effect (see, for example, [17-18]). Thus it can be thought that ions will most strongly influence the structures of those liquids in which the structure is most sensitive to variations in temperature. This latter can be characterized by the coefficients $\delta = \frac{1}{D_0}\frac{\partial D_0}{\partial T}$ and φ (Table 1), from a comparison of which it is clear that according to structural stability, H_2O and H_2O_2 occupy extreme positions. Thus the conclusions resulting from Equation (6) are in quantitative agreement with the structural properties of solvents.

The deviation of the experimental curve for ΔW for KCl in 99.99% H_2O_2 from curves for ΔW for NaCl, RbCl and CsCl, is, as we suppose, related to the fact that $K \approx 0$. A certain confirmation of this can be seen in the fact that in this case the sign of the derivative $\partial(\Delta W)/\partial\sqrt{c}$ is the same over the entire range of the ΔW curve as it is in all the remaining cases at the higher concentrations. Another confirmation results from the simplest model calculations, which show the possibility that $[U_c(r_{ij})]_{KCl} \approx 0$. Finally, it follows from data on the freezing point depression of H_2O_2 in the presence of NaCl [23] and of KCl [24], that Δt is larger in the KCl solutions, a fact which can serve as an indication of a smaller association in the KCl.

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THE APPLICATION OF THE ROTATING DISK ELECTRODE TO THE STUDY OF KINETIC AND CATALYTIC PROCESSES IN ELECTROCHEMISTRY

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(Presented by Academician A. N. Frumkin March 13, 1957)

In recent years, the development of the kinetics of electrochemical reactions has been marked by the initiation of a systematic study of those electrode reactions which proceed in such a way as to closely associate with accompanying chemical reactions in the body of the solution (kinetic and catalytic reactions). Up to the present time, the systematic study of these processes has been carried out with the aid of the dropping mercury electrode [1]. For this device, a general theory of catalytic and kinetic processes has been developed [1, 2].

As will be shown below, the rotating disk electrode, when used as a device for studying the kinetic and catalytic currents, has certain fundamental advantages over the dropping electrode. Thus, in distinction to the dropping electrode, processes on the rotating disk occur under stationary conditions. Due to this latter detail, working equations can be easily obtained for comparatively complicated reactions. The existence of such equations is a necessary prerequisite for the study of the rates of chemical reactions. In addition, the study of stationary processes is also simpler from the experimental standpoint. And, finally, it is possible in the case of the disk to vary the experimental conditions over wide intervals, altering not only the pH of the solution, but also the rate of rotation of the disk.

We will not attempt to take up all the variants of the different kinetic and catalytic processes. By some examples we will explain the characteristic technique of solving those problems which arise during the study of kinetic and catalytic processes.

As a first example [3], we will consider a kinetic process having a quasi-monomolecular character and proceeding according to the scheme:

$$\begin{array}{cc} \text{bulk} & \text{electrode} \\ A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B & A \rightarrow C \end{array}$$

This reaction is quasi-monomolecular in the sense that the velocity constant for the reaction B ⟶ A can here depend on the concentration of some one of the substances D, which are present in the solution:

$$k_2 = k_2 [D].$$

In what is to follow we will employ the notation:

$$k_2 = \rho, \quad k_1 = \rho\sigma, \ \text{where } \sigma = \frac{k_1}{k_2 [D]}.$$

If $C_1^{(0)}$ and $C_2^{(0)}$ designate, respectively, the concentrations of the substances A and B in the body of the solution and far removed from the electrode, the condition of equilibrium can then be written in the form

$$C_2^{(0)} - \sigma C_1^{(0)} = 0. \tag{1}$$

At the same time the total concentration of the solution has a fixed value:

$$C_1^{(0)} + C_2^{(0)} = C_0. \tag{2}$$

We will now consider the equations for the distribution of concentrations near the plane of the rotating disk, which serves as the reaction surface. In distinction to the body of the solution, equilibrium will be disturbed near the reaction surface, the substance A being consumed on the surface itself as the result of the electrode reaction.

The capacities of the volume sources of the substances A and B can be written as

$$Q_1 = \rho C_2 - \sigma\rho C_1, \quad Q_2 = -\rho C_2 + \sigma\rho C_1.$$

The equations for convectional diffusion in the presence of these volume sources can be [4] written as

$$V\frac{dC_1}{dy} = D\frac{d^2C_1}{dy^2} + \rho(C_2 - \sigma C_1), \tag{3}$$

$$V\frac{dC_2}{dy} = D\frac{d^2C_2}{dy^2} - \rho(C_2 - \sigma C_1). \tag{4}$$

In Equations (3) and (4) we have made use of a specific characteristic of a rotating disk, the entire surface of which is uniformly open to diffusion (supposing that edge effects are neglected), namely, that the concentration can be supposed independent of the coordinates $\underline{r}$ and φ. In addition, and for simplification of the calculations, we have considered the diffusion coefficients of the particles of A and B to be identical. In practice these values are frequently very close to one another. The case of unequal coefficients of diffusion is not in principle different from that which is considered below, but requires more lengthy calculations.

The relations (1) and (2) serve as the boundary conditions at infinity. We will now formulate the boundary conditions at the disk surface. We will suppose the electrode reaction to be very rapid, so that the concentration, C_1, of the substance A at the disk surface satisfies the condition

$$C_1 = 0 \quad \text{when } y = 0, \tag{5}$$

i.e., we limit ourselves to the case of the maximum diffusion current.

At the electrode the substance B is neither consumed nor produced. Thus its concentration, C_2, satisfies the condition

$$\frac{dC_2}{dy} = 0 \quad \text{when } y = 0. \tag{6}$$

For the solution of this system it is convenient to introduce the new unknown functions

$$\varphi = \rho(C_2 - \sigma C_1), \quad \psi = C_1 + C_2.$$

Simple calculations lead to the following equations for the functions ψ and φ:

$$V\frac{d\psi}{dy} = D\frac{d^2\psi}{dy^2}, \tag{7}$$

from which it follows that

$$\psi = a_1\int_0^y \exp\left\{\int_0^t \frac{V(t')\,dt'}{D}\right\} dt + a_2, \tag{8}$$

$$V \frac{d\varphi}{dy} = D \frac{d^2\varphi}{dy^2} - \alpha\varphi, \tag{9}$$

with $\alpha = \rho(1 + \sigma)$.

For the solution of Equation (9), we will suppose the volume chemical reaction to be rapid, so that the inequality

$$V \frac{d\varphi}{dy} \ll \alpha\varphi. \tag{10}$$

is always valid.

For φ it is then possible to write

$$\varphi = \text{const} \cdot \exp\left[-\sqrt{\frac{\alpha}{D}}\, y\right]. \tag{11}$$

With the aid of this expression for φ, the boundary conditions for ψ can be obtained from (5) and (6) in the form

$$\psi \to C_0 \text{ when } y \to \infty, \quad \left(\frac{d\psi}{dy}\right)_{y=0} = \frac{1}{\sigma} \sqrt{\frac{\alpha}{D}}\, \psi.$$

Making use of the general solution of the boundary value problem for ψ [4], we find the final form of the functions ψ and φ. The total reaction rate is given by the diffusion current at the disk surface. A calculation with the aid of the relations which have been obtained in [4], gives

$$j = D\left(\frac{dC_1}{dy}\right)_{y=0} = D\left(\frac{d\psi}{dy}\right)_{y=0} = \frac{DC_0}{1{,}61\left(\frac{D}{\nu}\right)^{1/3}\sqrt{\frac{\nu}{\omega}}} \; \frac{1}{\left[1 + \frac{\sigma}{1.61}\sqrt{\frac{\omega}{\alpha}\left(\frac{D}{\nu}\right)^{1/3}}\right]}, \tag{12}$$

ω being the angular velocity of rotation of the disk and ν the kinetic viscosity of the solution.

Introducing the descriptive concepts of the depths of the diffusion layer, δ', and the kinetic layer, δ_k, [5], it is then possible to write j as

$$j = \frac{DC_0}{\delta'(1 + \delta_{\kappa}/\delta')},$$

where $\delta_k = \sqrt{D/\alpha}$ and δ' has the value which was calculated in [4]. The condition for the applicability of the approximation (10) is obtained from an evaluation of terms of successive orders, infinitesimals. Calculation gives in place of (10)

$$\frac{1}{8}\sqrt{\frac{\omega^2}{\alpha^3}\left(\frac{D}{\nu}\right)} \ll 1. \tag{13}$$

The inequality (10) can be concretely interpreted if it is written in the form

$$\delta_{\kappa} \ll \delta. \tag{14}$$

An analogous case has been considered in the work of Budevsky [6]. He, however, assumed that the liquid was immobile throughout a diffusion layer of fixed depth.

We will now consider another typical example of a kinetic process [7]. We will suppose that the volume reaction proceeds in accordance with the scheme

$$2\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

and has, therefore, bimolecular character. Here the source strengths are of the form

$$Q_1 = k_2C_2 - k_1C_1^2, \quad Q_2 = {}^1/_2\,(k_1C_1^2 - k_2C_2).$$

The coefficient $^1/_2$ indicates that from the consumption of one molecule of the substance A there arises $^1/_2$ molecule of the substance B.

In this case the concentration distributions of the substances A and B are determined by the equations

$$V\frac{dC_1}{dy} = D\frac{d^2C_1}{dy^2} + k_2C_2 - k_1C_1^2, \tag{15}$$

$$V\frac{dC_2}{dy} = D\frac{d^2C_2}{dy^2} - \frac{\kappa_2C_2}{2} + \frac{1}{2}k_1C_1^2. \tag{16}$$

The boundary conditions at infinity can be written as

$$k_1C_1^{(0)} - k_2C_2^{(0)} = 0 \text{ when } y = \infty; \tag{17}$$

$$C_1^{(0)} + C_2^{(0)} = C_0. \tag{18}$$

This last equation obviously expresses the condition for equilibrium. We will consider that the velocity constant for the reaction B ⟶ 2A is large in comparison with that for the reverse reaction, so that in the body of the solution the inequality

$$C_2^{(0)} \gg C_1^{(0)}.$$

is valid.

The boundary condition (18) can then be written as

$$C_2^{(0)} \simeq C_0 \text{ when } y \to \infty. \tag{19}$$

Limiting ourselves, as before, to the case of a very rapid electrode reaction, it is possible to consider the boundary conditions on the disk surface as having the forms (5) and (6).

For the solution of the system of equations (15) and (16) we will introduce the new unknown function

$$\psi = C_1 + 2C_2,$$

which satisfies Equation (7). Expressing C_2 in terms of ψ and C_1, we can write (15) as

$$V\frac{dC_1}{dy} = D\frac{d^2C_1}{dy^2} + k_2\frac{\psi - C_1}{2} - k_1C_1^2. \tag{20}$$

Supposing, just as in the case of the monomolecular reaction which was considered above, that the rate of the volume chemical reaction is sufficiently great so that the convection term can be neglected in (20), and considering that the variation of the function ψ occurs at the depth of the diffusion layer δ', and the variation of C_1 thoughout the kinetic layer of depth δ_k, it is possible to obtain a first integral of (20).

Making use of the integral of (20), the boundary conditions for ψ can be formulated as

$$\psi \rightarrow 2C_0 \text{ when } y \rightarrow \infty; \tag{21}$$

$$\frac{d\psi}{dy} = k\psi^{3/4} \text{ when } y = 0, \tag{22}$$

where

$$k = \left(\frac{k_2^3}{k_1 D^2}\right)^{1/4} \frac{1}{\sqrt[4]{18}}.$$

The solution of such a boundary value problem has been obtained earlier in [4]. The diffusion current is equal to

$$j = D \frac{2C_0 - \psi_{y=0}}{1.61\,(D/\nu)^{1/3} \sqrt{\nu/\omega}}, \tag{23}$$

$\psi_{y=0}$ satisfying the algebraic equation

$$\psi_{y=0}^{3/4} + \frac{D}{k\delta'} (\psi_{y=0} - 2C_0) = 0. \tag{24}$$

The condition for the applicability of the derived equations is the fulfillment of the inequality

$$\left(\frac{\omega}{\sqrt{k_1, k_2, C_0}}\right)^{2/3} \left(\frac{D}{\nu}\right)^{1/3} \ll 1. \tag{25}$$

For the disk there is no great difficulty in the analysis of more complex situations, such as the case of a slow electrode reaction.

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SURFACE PHENOMENA IN THE TERNARY METALLIC SOLUTIONS
Hg–Cd–K AND Hg–Cd–Cs AT 22°

P. P. Pugachevich and V. B. Lazarev

(Presented by Academician I. I. Chernyaev May 16, 1957)

In [1] we have shown that an effect of concentration buffering, analogous to that observed for binary dielectric mixtures in the presence of electrolytes, is met in the ternary Hg–Cd–K metallic solutions in which cadmium and potassium oppositely influence the surface tension of mercury.

With the aid of the composite apparatus of [2], we have up to the present studied the 22° surface tensions (σ) of 135 Hg–Cd–Cs solutions, these containing from 0 to 6.98 at. % of cadmium and from 0 to 0.036 at. % cesium, and have detected concentrating buffering in this system also (Figs. 1 and 2).

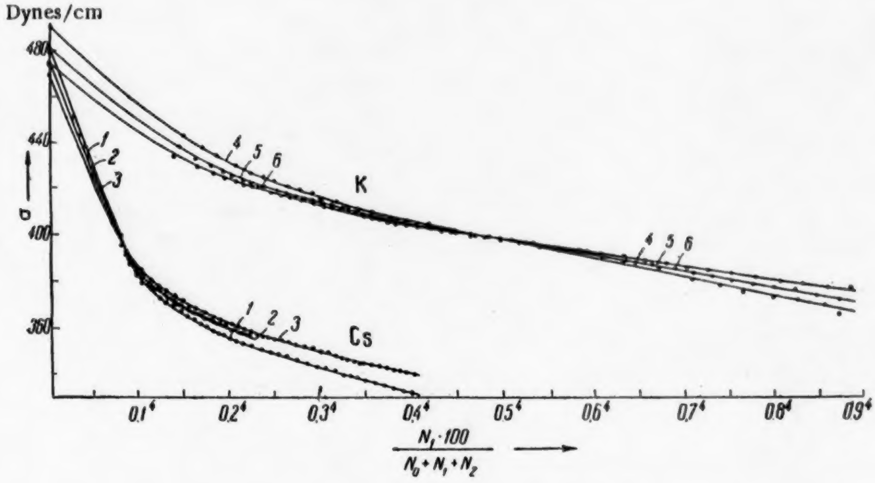


Fig. 1. The surface tensions of Hg–Cd–K and Hg–Cd–Cs solutions at 22°. Cadmium concentrations: 1) 6.98; 2) 3.78; 3) 1.32; 4) 7.13; 5) 5.52; 6) 1.61 at. %.

A comparison of the surface tension isotherms for the ternary metallic solutions (Fig. 1) with the isotherms for aqueous solutions of alcohols in the presence of electrolytes (Fig. 3) makes it possible to obtain additional confirmation for the basic conclusion, resulting from the V. K. Semenchenko molecular theory of surface phenomena [4-6], of the generality of the adsorption laws for multicomponent solutions belonging to various classes.

Actually, as is clear from Figs. 1 and 3, in ternary metallic solutions, just as in aqueous solutions of dielectrics in the presence of surface-inactive components, the buffer point is displaced in the direction of lower concentrations as the surface-active component of a given solution is replaced by another component possessing greater surface activity.

Seith [7] considered that concentration buffering is related to hydration or, in the general case, to solvation of the molecules of the surface-inactive substance; he surmised that the concentration of the surface-active substance in the surface layer was here independent of the concentration of the surface-inactive substance in the system. This explanation cannot, however, be considered satisfactory [6] and it is definitely not applicable to metallic solutions.

V. K. Semenchenko [4-6] has developed a molecular theory of surface phenomena in multicomponent solutions, in which qualitative predictions concerning many surface properties of such solutions can be formulated and, in particular, an explanation given for the effect of concentration buffering. Actually, starting from the Gibbs adsorption equation, the Gibbs-Duhem relation for real ternary solutions and the V. K. Semenchenko expressions for adsorption [6], it is possible to show [8] that the derivative of the surface tension with respect to the concentration, C_{N_2}, of the surface-inactive substance, expressed in atomic fractions; i. e., $(\partial\sigma/\partial C_{N_2})_{C_{N_1}}$ changes its sign as the concentration, C_{N_1}, of the surface-active additive increases, and passes through the value zero. The concentration of the surface-active material at which $(\partial\sigma/\partial C_{N_2})_{C_{N_1}} = 0$, is that corresponding to the buffer concentration:

$$C_{N_1}^{\text{buf.}} = -\frac{\left[e^{\frac{\gamma}{kT}(m_0-m_2)}-1\right]\left(1+C_{N_2}\frac{\partial f_2}{\partial C_{N_2}}\right)}{\left[e^{\frac{\gamma}{kT}(m_0-m_1)}-1\right]\frac{\partial f_1}{\partial C_{N_2}}}, \tag{1}$$

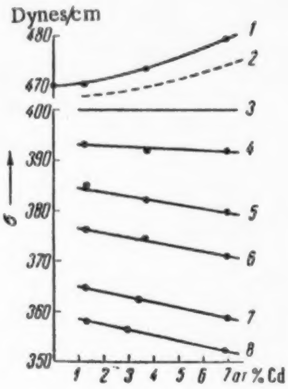
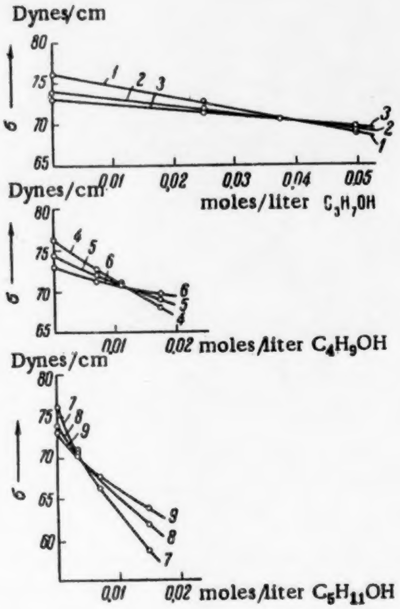


Fig. 2. The surface tensions of Hg–Cd–Cs solutions at 22°. Concentrations of cesium: 1) 0.00000; 2) 0.0000025; 3) 0.0000041; 4) 0.000055; 5) 0.00011; 6) 0.00028; 7) 0.0011; 8) 0.0025 at. %.



m_0, m_1 and m_2 being the generalized moments of the solvent, the surface-active and the surface-inactive substances and f_1, f_2 the activity coefficients for the surface-active and the surface-inactive substances.

Fig. 3. The surface tensions of aqueous solutions of alcohols in the presence of NaBr at 18°, according to the data of V. K. Semenchenko and E. A. Davidovskaya [3]. Concentrations of NaBr: 1) 1.9; 2) 0.5; 3) 0.0; 4) 1.9; 5) 0.95; 6) 0.0; 7) 1.9; 8) 0.5; 9) 0.0 moles/liter.

As is to be seen from Equation 1, the passage to a substance with greater surface activity in a ternary system for which $m_0 - m_2$ = const. moves the buffer point toward the region of lower concentrations, a fact which is supported by the experimental results (Figs. 1 and 3).

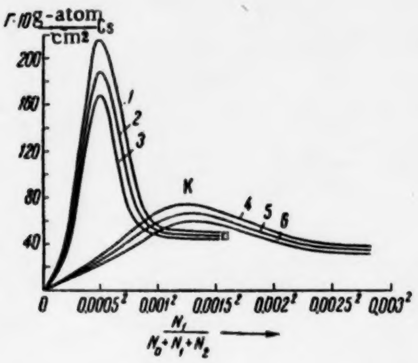


Fig. 4. The adsorption of potassium and cesium in Hg–Cd–K and Hg–Cd–Cs solutions at 22°. Concentrations of cadmium: 1) 6.98; 2) 3.78; 3) 1.32; 4) 7.13; 5) 5.52; 6) 1.61 at. %.

It also follows from the V. K. Semenchenko theory that in a ternary system, one of whose components is surface-active with respect to the solvent and the other surface-inactive, the adsorption of the former will be positive and will pass through a maximum. This maximum value of the adsorption increases with the concentration of the surface-inactive substance. The theory also affirms that in such a system the maximum adsorption of the surface-active substance will be the greater, the greater its surface activity, whereas the concentration corresponding to this maximum will diminish with a rise in the surface activity of this surface-active additive. With the aid of graphic differentiation, and using the equation proposed by V. K. Semenchenko [6],

$$\Gamma_1^N = \frac{1}{RT}\left[C_{N1}\left(\frac{\partial\sigma}{\partial \ln C_{N\,2}}\right)_{C_{N1}} - (1 - C_{N\,1})\left(\frac{\partial\sigma}{\partial \ln C_{N1}}\right)_{C_{N2}}\right] \qquad (2)$$

we have calculated the adsorption, Γ_1^N, of the surface-active components in those ternary metallic solutions of Hg–Cd–K and Hg–Cd–Cs which have been studied by us, and have found (see Fig. 4) that the conclusions of the V. K. Semenchenko theory [4-6] concerning the laws of adsorption in multicomponent systems are in complete agreement with the experimental results on ternary metallic solutions.

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** In Russian.

PROTON RESONANCE IN NONAQUEOUS SOLUTIONS OF PARAMAGNETIC SALTS

A. I. Rivkind

(Presented by Academician A. E. Arbuzov April 24, 1957)

1. In [1, 2] there has been pointed out the influence of an amply stable close order in the neighborhood of the paramagnetic particles (solvation of ions) and a rapid hydrogen exchange between the protons of the solvent molecules (water) on the character of the proton resonance in a paramagnetic solution. In aqueous solutions it proves to be so that the hydrate envelopes do not screen the paramagnetic ions from the protons of the solvent; due to the rapid hydrogen exchange,each of the protons will succeed in penetrating into a solvation layer of water molecules within a time $\lesssim T_1$ (T_1 is the time of magnetic relaxation of the proton and is equal to $10^{-2} - 10^{-4}$ seconds) and exist temporarily at the distance of closest approach to the paramagnetic ion. In other words, the hydrogen exchange makes the hydrate atmosphere around the ion sufficiently "transparent" for the protons of the solvent, so that it can be effectively penetrated by these during the time T_1 of the relaxation cycle. Thus in aqueous solutions the existence of close order has as its only result the fact that, within a certain distance from a paramagnetic ion, it is not the thermal movement of the water molecules which predominates in velocity but the alteration of the orientation of the electrons relative to an externally imposed static magnetic field, H_0, this proceeding with a characteristic time $\rho/2\pi$ (ρ being the time of paramagnetic relaxation of the electron). In order of magnitude this time, $\rho/2\pi$, amounts to 10^{-8} sec or less, depending on the type of ion, and proves always to be shorter than the characteristic time for the hydrogen exchange. Concrete instances of this molecular mechanism in experiments on proton resonance have been considered in [1, 2].

2. In connection with the above, it seemed of interest to investigate proton resonance in paramagnetic solutions where rapid hydrogen exchange was either lacking or, if it did occur, involved the participation of only a small portion of the protons of the solvent. In such a solution it was presumed that the presence of "impenetrable" solvation atmospheres around the paramagnetic particles (in the sense which has been indicated in Par. 1) would lead to a sharp rise in the relaxation time T_1 because of the marked increase in the distance of proton-ion approach. It has proven possible to actually observe this in practice.

As experimental substances there were selected absolute (dehydrated) acetone and alcohol solutions of the crystal hydrates of the paramagnetic salts of the elements of the iron group.* In the acetone solutions, the protons, all of which are found in the C-H bonds of the acetone molecules, are incapable of rapid hydrogen exchange; in the alcohol solutions, rapid hydrogen exchange is carried on only by the hydroxyl protons of the alcohol molecules, i. e., by $\frac{1}{6}$ of all the solvent protons.

The apparatus and the technique which had been employed in [1, 2]** were used for carrying out the measurements. All of these experiments were performed at room temperature and in a fixed magnetic field, $H_0 \sim 2300$ oersted.

3. In Table 1 there are presented the results of measurements on the acetone solutions.

In this table there are listed mean values of the product $T_1 N$ over the investigated ranges of concentration (N is the concentration of the solution) and of $T_1/T_{1\,aq}$, the ratio of the relaxation time in acetone solution to the relaxation time in an equimolar solution of the same salt. It is to be seen from the data of Table 1 that the dissolved paramagnetic salt comparatively weakly affects the relaxation of the protons in acetone and T_1 is considerably greater than $T_{1\,aq}$. The affect due to salts of the trivalent ions (in solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$) is especially insignificant.

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* In [1] mention was made of results on acetone solutions of salts of divalent manganese and copper. The attempt which was there made to explain the observed unevenly long times of relaxation, T_1, of these solutions is not, however, justified by the accumulated experimental data of the present work.

** A detailed description of the experimental technique is contained in [3].

The dependence of the relaxation time of the protons, T_1, on the electrical charge of the paramagnetic particles, is qualitatively a new effect which is not peculiar to the aqueous solutions of the paramagnetic salts. The picture becomes clearer if we pass from T_1 to another relaxation parameter, the effective magnetic moment, μ_{eff}, [4] (see Table 1). Values of μ_{eff} have been calculated according to the equation [4]

$$1/T_1 = C\mu^2_{eff}N,$$

where C is a coefficient which includes the temperature dependence. Values of μ_{eff} for Table 1 were obtained from this equation by using a coefficient C which was arbitrarily so chosen that the condition $\mu_{eff_1} = \mu_{st} = 5.9\mu_B$ (μ_{st} is the static magnetic moment from measurements of the susceptibility of aqueous solutions)* would be fulfilled for acetone solutions of $Mn(NO_3)_2 \cdot 6H_2O$. The values which are thereby obtained for the copper salts are also such that $\mu_{eff_1} \cong \mu_{st}$, but for the solutions of the salts of the trivalent ions (Fe, Cr) μ_{eff_1} proves to be strongly reduced in comparison with the corresponding static value (see Table 1). If, on the other hand, it is assumed that the effective and static moments are equal for acetone solutions of $Fe(NO_3)_3 \cdot 9H_2O$ (see μ_{eff_2} in Table 1), then for the solutions of the second trivalent ion, chromium, $\mu_{eff_2} \cong \mu_{st}$ also results, but for solutions of the salts of the divalent ions, manganese and copper, $\mu_{eff_2} \gg \mu_{st}$.** The acetone solutions of the salts of cobalt and nickel deviate from this rule; for these it proves to be so that $\mu_{eff_1} \ll \mu_{st}$, $\mu_{eff_2} \ll \mu_{st}$. A similar situation has also been noted in the study of the aqueous solutions of these salts [4-6]. The fundamental cause of this is, in all likelihood, the exceptionally rapid relaxation of the electron spins of Co^{2+} and Ni^{2+} ($\rho \lesssim 10^{-11}$ sec.).***

TABLE 1

Relaxation Parameters of the Protons in Acetone Solutions of Paramagnetic Salts
($H_0 \sim 2300$ oersteds; $T \sim 290°K$)

Salt	Interval of concentrations, in moles/liter	$T_1N \cdot 10^3$ in sec.moles//liter	$T_1/T_{1\,aq}$	μ_{eff_1} in units μ_B	μ_{eff_2} in units μ_B	μ_{st}, in units μ_s (from measurements on aqueous solutions)
$Cr(NO_3)_3 \cdot 9H_2O$	0.05—0.1	0.87±0,02	45	2.66	3.79	3.8
$Mn(NO_3)_2 \cdot 6H_2O$	0.02—0.05	0.177±0,002	12.3	5.9**	8.4	5.9
$Fe(NO_3)_3 \cdot 9H_2O$*	0.01—0.05	0.36±0,00	25	4.14	5.9**	5.9
$Co(N_3O)_2 \cdot 6H_2O$	0.15—0.5	5.8±0,5	7.68	1.03	1,47	5,0
$Ni(NO_3)_2 \cdot 6H_2O$	0.2 —0.5	4.62±0,25	15.6	1.15	1.65	3.1
$Cu(NO_3)_2 \cdot 3H_2O$*	0.05—0.5	1.43±0,09	12.5	2,07	2.96	2.0
$CuCl_2 \cdot 2H_2O$	0.025—0.1	1.46±0,07	12.8	2.05	2.92	2.0

* Salts, solutions of which were acidified with concentrated acetic acid in order to avoid hydrolysis.

** Arbitrary.

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* Within those limits of precision which are of significance in a comparison of μ_{eff} and μ_{st}, we consider it permissible to employ μ_{st}'s from measurements in aqueous solutions.

** It should be emphasized that as the result of the arbitrary value of the coefficient C, all of the values of μ_{eff_1}, and μ_{eff_2} in Table 1 have a purely conventional character and are intended only for comparing the intensities of the effects of the paramagnetic salts on the relaxation of protons in a single solvent, acetone.

*** For aqueous solutions this has been definitely proven in [1].

Regularity in the dependence of the relaxation time, T_1, on the charge of the paramagnetic particles in acetone solutions of chromium, manganese, iron and copper, is not accidental. The same is true of the large times, T_1, which are obtained for all of the acetone solutions ($T_1/T_{1\,aq} \gg 1$); this points to the existence of solvates which are impenetrable (at least within a time $\lesssim T_1$) for the protons of the solvent. The higher the charge of the paramagnetic ion, the greater is the depth of the solvate layer, and accordingly the larger must be the distance of proton approach. As a result, the magnetic dipole interaction between these particles proves to be correspondingly weakened, the relaxation time, T_1, thereby increasing.

Finally, we will consider one other peculiarity of the relaxation in acetone solutions. On the basis of the example of the antipyrine complexes of trivalent iron, the effect of chemical complex formation was studied. In distinction to the aqueous solutions, in which the screening of the Fe^{3+} ions by the molecules of antipyrine brings about a six fold increase in the time T_1 [3], in acetone solutions of $Fe(NO_3)_3 \cdot 9H_2O$ it is found that the formation of complexes with antipyrine is almost without influence on the relaxation time.

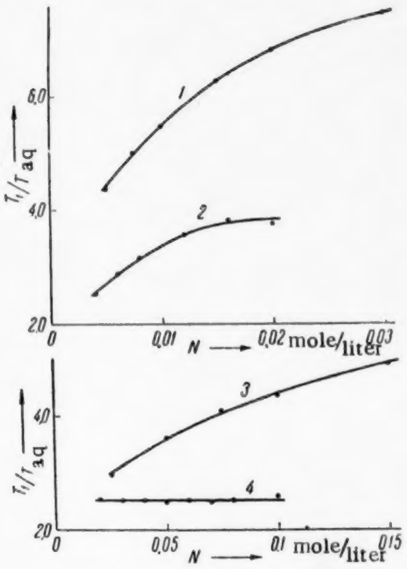

Fig. 1. The ratio between the relaxation time in alcohol solutions, T_1, and the relaxation time in equimolar aqueous solutions, T_{1aq}, as a function of the solution concentration, N, 1) solution of the salt $Fe(NO_3)_3 \cdot 9H_2O$; 2) $Mn(NO_3)_2 \cdot 6H_2O$; 3) $CuCl_2 \cdot 2H_2O$; 4) $CuCl_2$. In order to avoid hydrolysis, the alcohol solutions of $Fe(NO_3)_3 \cdot 9H_2O$ were acidified with concentrated nitric acid.

The explanation here similarly follows from what has been said above: the basic mass of protons, not being in a position to penetrate into the solvation layers of acetone molecules, "does not know about" changes which are occurring in the immediate neighborhood of the paramagnetic particles. Supposing a proportionality between T_1 and the cube of the effective distance of proton-ion approach [1], we find that the solvate atmosphere in an acetone solution is, in its screening action, approximately equivalent to a stationary envelope of two or three layers of solvent molecules.

4. From this point of view, the results of the measurements on alcohol solutions also become understandable. Even here, the ratio $T_1/T_{1\,aq}$ for solutions of salts of trivalent iron is much greater than for the solutions of the salts of divalent manganese (Fig. 1, 1 and 2), despite an approximate equality between their static moments. Just as in the acetone solutions, the ratio $T_1/T_{1\,aq}$ is especially high for solutions of trivalent chromium (for alcohol solutions of $CrCl_3 \cdot 6H_2O$, $T_1/T_{1\,aq} \simeq 14.2$). There is also observed an anomalously low effectiveness in the salts of cobalt, nickel, etc.

An important special characteristic of the alcohol solutions is the fact that for them the ratio $T_1/T_{1\,aq}$ diminishes precipitately with a decrease in the concentration N (Fig. 1, 1, 2, 3). It is obvious that in dissolving crystal hydrates in absolute alcohol, a considerable amount of the water of crystallization is held in the inner coordination spheres of the paramagnetic particles, thus aiding the formation of more highly dissociated and, accordingly, better solvated, ionic forms. As N decreases, there is a diminution of the total amount of water which is introduced into solution, as a result of which a larger and larger share of it is taken up by the alcohol. This leads to a decrease in the degree of dissociation and to a corresponding diminution in the time T_1. It is characteristic that the crystal hydrates of trivalent chromium, which firmly coordinate water, [7], give alcohol solutions for which $T_1/T_{1\,aq} \simeq$ const. up to the very highest dilutions.

In addition to the solutions of the crystal hydrates, alcohol solutions of anhydrous cuprous chloride were also investigated (Fig. 1, 4). As was to be expected, for these solutions the ratio T_1/T_{1aq} does not depend on the concentration N and shows the same value as that to which $T_1/T_{1\,aq}$ for the alcohol solutions of $CuCl_2 \cdot 2H_2O$ tends with decreasing concentration.

Although only one proton (the hydroxyl) in the alcohol molecule participates in the rapid hydrogen exchange, the ratio $T_1/T_{1\,aq}$ for the alcohol solutions is, as a rule, several times lower than that for the acetone solutions. It can be supposed that the indirect magnetic interaction of the hydroxyl proton with the remaining protons of the molecule [8] essentially fixes the position of their spin temperature, T_s.

The results of this work indicate that for proton resonance in paramagnetic solutions which do not show rapid hydrogen exchange between all, or a large part, of the protons, those effects which are related to the existence of close order in the immediate neighborhood of the paramagnetic particles are very crudely manifest in determining both the character of the behavior and the order of magnitude of the measured relaxation parameters.

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THE REACTIVITY OF FIVE- AND SIX-MEMBERED HETEROCYCLIC COMPOUNDS

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(Presented by Academician A. A. Balandin May 25, 1957)

Many instances are known of five-membered heterocyclic compounds which prove to be considerably more reactive than the six-membered compounds of the same series. Thus tetrahydrofuran is more active than tetrahydropyran, the five-membered glucosides prove to be many times more reactive than the six-membered ones and the five membered γ-monosaccharides, in distinction to the six-membered, are so unstable that they cannot be prepared in the free condition and exist only in the form of derivatives.

It is natural to seek in thermodynamics for the cause of this difference in reactivity in the compounds of a given homologous series. To confirm this statement the change of the free energy should be evaluated in corresponding reactions. Unfortunately this is, at the present time, a difficult task, principally because of the lack of data on entropies. In the case of the lactams and the formals [1, 2] it has been shown, however, that the ability to polymerize changes in parallel with the so-called enthalpy of ring formation, i. e., with the difference between the enthalpy of a given cyclic compound and the additively calculated enthalpy of the unit in the corresponding polymer. From this it follows that the enthalpy of ring formation can, in a certain degree, characterize the reactivity of a given cyclic compound with respect to its transformation into linear compounds.

It is the basic problem of this work to extend this result to the γ- and δ-forms of the monosaccharides, substances, the polymerization of which, plays a considerable role in the biosynthesis of natural compounds. In addition, we have succeeded here in elucidating certain other questions which, as we see it, are of fundamental interest.

For a given cyclic compound the calculation of the enthalpy of ring formation can be carried out in two ways: 1) by a comparison of the experimentally determined heat of combustion of this compound with its heat of combustion as calculated additively in terms of increments due to the respective groups; 2) by a comparison of the heats of combustion of the five- and the six-membered compounds of the series in question.

If it is supposed that the enthalpy of ring formation of the six-membered cycle is equal to zero, as has proven to be the case in many instances, it is then possible to determine the enthalpy of ring formation for the five-membered cycle from the equation:

$$-\Delta H_{rf} = (-\Delta H_{\text{comb. 5 m}} + A) - (-\Delta H_{\text{comb. 6 m}}),$$

A being the increment in the heat of combustion due to that group by which the 6- and the 5-membered cycles differ.

Thus the experimentally determined values are the heats of combustion of the respective compounds. These heats of combustion have been reduced to the gaseous state in all of those cases where this proved to be possible. Heats of vaporization have been calculated by empirical and semi-empirical equations [3-5].

The calorimetric apparatus and the technique of measuring the heats of combustion have been described in detail earlier [6]. With the exception of n-dibutyl ether, the heats of combustion of the investigated substances, both liquid and solid, have been obtained with an accuracy of 0.2-0.3% (average deviation from the arithmetic mean). The liquid substances were burned in thin-walled glass ampules, weighing 0.15-0.25 g. Some of the materials for this study, namely: α-D- and β-D-CH_3-glucopyranosides (δ-form), β-D-CH_3-glucofuranoside (γ-form) and 2-methoxytetrahydropyran were synthesized by us. Methods for preparing these substances are described in the literature [7-10]. The remaining materials were available in the prepared form and were merely subjected to a careful purification. The physico-chemical constants were determined for all of these substances and their values agreed well with the data of the literature. In Table 1 there are listed the heats of combustion of all of those substances which we have studied.

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* Deceased.

In the second column of Table 1 there are given, in $\text{kcals}_{15°}$, the enthalpy changes accompanying isothermal (20°) combustion of the studied materials in the solid or liquid state, at a pressure of 1 at. and with the formation of gaseous CO_2 and liquid H_2O, also at 1 at., as combustion products. In the third column there are shown the calculated heats of vaporization and, in the last column, the heats of combustion in the gaseous state.

TABLE 1

Substance		$-\Delta H_c^{20}$, kcal/mole	Heat of vaporization, kcal/mole	$-\Delta H_c^{20}$ (g), kcal/mole
Tetrahydrofuran	(l)	598.0±0.1	7.8	605.8
Tetrahydropyran	(l)	750:1±0.2	8.5	758.6
n-Dibutyl ether	(l)	1277.5±0.8	11.2	1288.7
α-D-glucose	(s)	670.3±0.1	—	—
2-Methoxytetrahydropyran	(l)	868.8±0.3	10.2	879.0
δ-Oxyvaleraldehyde	(l)	697.2±0.2	—	—
α-D-Xylose	(s)	559.2±0.2	—	—
α-D-Methylglucopyranoside	(s)	842.1±0.2	—	—
β-D-Methylglucopyranoside	(s)	841.1±0.1	—	—
β-D-Methylglucofuranoside	(l)	849.4±0.2	—	—

The data obtained by us make it possible to draw a number of conclusions.

1. For the example of the simplest oxygen-containing heterocycles, tetrahydropyran and tetrahydrofuran, a comparison of the experimental and the additively calculated heats of combustion makes it possible to show that the enthalpy of ring formation for the 6-membered cycle is approximately zero, while that for the 5-membered cycle amounts to about 5 kcal (for the cyclanes and for the cyclic formals this has been proven earlier [2]). The increment per atom of oxygen (−28.8 kcal/mole) which is required for additive calculations is evaluated from the difference between the heats of combustion of n-dibutyl ether and n-octane [11]. The increment per $-CH_2-$ group is set equal to 157.4 kcal/mole [11]. The calculation is carried out for the gaseous state following the two above-mentioned procedures.

a. The enthalpy of ring formation, $-\Delta H_{rf}$, $= -\Delta H_{\text{comb. exp.}} - (-\Delta H_{\text{comb. add}})$, where $-\Delta H_{\text{comb. add.}} = 157.4\,n + (-28.8)$ and n is the number of $-CH_2-$ groups. Through such calculations, the value of $-\Delta H_{rf}$ for tetrahydropyran proves to be equal to 0.4 kcal/mole ($758.6_{\text{exp.}} - 758.2_{\text{add}}$), and that for tetrahydrofuran, to 5 kcal/mole (605.8-600.8).

b. For the 5-membered cycle, the enthalpy of ring formation can also be calculated from the following relation:

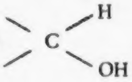
$$-\Delta H_{rf} = (-\Delta H_{\text{comb. 5 m}} + 157.4) - (-\Delta H_{\text{comb. 6 m}}) = (605.8 + 157.4) - 758.6 = 4.6 \text{ kcal/mole}$$

The results obtained in these two cases are close to one another, due to the fact that the experimental and calculated heats of combustion of tetrahydropyran almost coincide.

2. On passing to the determination of the heats of combustion of the carbohydrates and of substances which are closely related to these in structure, we considered it necessary to test the method for some pure material of this type. α-D-glucose was selected for this purpose. According to our measurements (see Table 1), the heat of combustion of the latter is $-\Delta H_C^{20} = 670.3$ kcal/mole; from the data of Huffman and Fox [12], as reduced to our conditions, it is $-\Delta H_C^{20} = 670.18$ kcal/mole. The difference amounts to 0.02%.

3. It was further necessary to show the validity of the simplest additive calculations for carbohydrates containing a large number of functional polar groups in the molecule. For this purpose heats of combustion were determined for 2-methoxytetrahydropyran, δ-oxyvaleraldehyde, α-D-CH_3-glucopyranoside and α-D-xylose and the following calculations were then carried out:

a. The increment for the replacement of a hydrogen atom on the first carbon by a methyl radical was computed by comparing the heats of combustion for 2-methoxytetrahydropyran and δ-oxyvaleraldehyde: 868.8--697.2 = 171.6 kcal/mole and for α-D-CH_3-glucopyranoside and α-D-glucose: 842.1-670.3 = 171.8 kcal/mole. In this case, change in the ring structure is without effect on the magnitude of the increment.

b. On the basis of the data on the heat of combustion of α-D-xylose, there was calculated the heat of combustion of α-D-glucose. The increment per  group (111.8 kcal/mole) was evaluated by comparing the heats of combustion of n-hexanol (950.6 kcal mole) and n-pentane (838.8 kcal mole) in the liquid state [11, 13]. The calculated value proved to be 671.0 kcal/mole; the experimental, 670.3 kcal/mole.

Similar calculations have shown the possibility of applying the simplest additive calculations to the class of carbohydrates.

4. Thus, in the case of the carbohydrates, it can be considered that the enthalpy of ring formation will be approximately zero for the 6-membered cycle. This permits the evaluation of the enthalpy of ring formation for the 5-membered β-D-CH_3-glucofuranoside cycle by comparing its heat of combustion with the heat of combustion of the 6-membered β-D-CH_3-glucopyranoside (849.4-841.1 = 8.3 kcal/mole). However, in view of the difference in the states of aggregation of the compared substances the resulting value cannot be looked on as the enthalpy of ring formation for β-D-CH_3-glucofuranoside. It is possible to set the enthalpy of crystallization of β-D-CH_3-glucopyranoside equal to the enthalpy of crystallization of α-D-CH_3-glucopyranoside, which, according to the data of the literature, amounts to about 3 kcal/mole [14]. Then the enthalpy of ring formation for the 5-membered cycle (γ-form) amounts to about 5 kcal/mole. This permits an explanation of the enhanced reactivity of the 5-membered cycles (in the case of the hydrolysis of these compounds, for example, the impossibility of separating the γ-monosaccharides (the furanoses) in the free state) and gives a certain degree of justification to the hypothesis that it is possible that the higher carbohydrates are formed in nature by the polymerization of the corresponding low molecular cyclic compounds.

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AN ELECTRICAL RESISTANCE METHOD FOR INVESTIGATING POWDERED METALLIC CATALYSTS IN THE LIQUID PHASE

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V. V. Malakhov

In a series of papers [1] it has been pointed out that once the potential at the electrodes has reached a definite "critical" value there is a possibility of forming conducting "bridges" in suspensions of conductors and semiconductors in dielectrics. For platinum, conduction has been observed even at $E_{crit} = 20$ V/cm.

Through measurements of the resistance of platinum suspensions, we have convinced ourselves of a variation in this quantity ranging from several, up to hundreds of ohms. It was impossible to obtain reproducible values. On the other hand it has been noted that the resistance of a suspension becomes regular as sedimentation proceeds in it. In this connection there arose the thought of measuring the resistance of metallic powders after sedimentation.

As test materials there were selected Raney nickel and platinum black; n-heptane, which possesses a low specific conductivity ($1 \cdot 10^{-13}$ ohm^{-1} · cm^{-1}) was chosen as the solvent. Experiments were also carried out in benzene, 96% alcohol and glacial acetic acid.

At the base of the cell which was used in determining the electrical conductivity of the powders, there was placed a catalytic hydrogenation flask. At the level of the bottom of the latter there were welded the electrodes, two platinum wires, each 6 cm in length, separated by a distance of 5 mm. Resistance measurements were carried out with a direct-current bridge of the UMV type, under the potential of a 6 v battery.

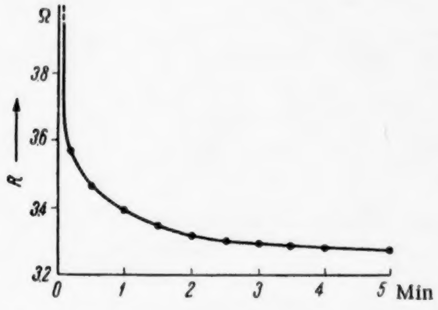

Fig. 1. The variation in the resistance of Raney nickel during sedimentation.

It turned out that the high conductivity of the active nickel powder resulted from the presence of hydrogen in it. In freshly prepared Raney nickel the resistance can vary from several, up to thousands of ohms, whereas a powder which has stood under alcohol for several days can completely fail to conduct the current. On saturating the powder with hydrogen, however, the resistance falls as long as the hydrogen is being adsorbed, finally reaching a fixed, low value which we have provisionally designated as the "saturation resistance."

The system does not conduct the current on being agitated, but even 10 seconds after the agitation has ceased, it is possible to measure a resistance in the powder, this resistance gradually diminishing with time (Fig. 1).

This change is tied up with the compacting of the resulting precipitate and with the increase in the total number of precipitated particles as well.

The resistance of the Raney nickel is directly proportional to the distance between the electrodes and diminishes regularly with an increase in the charge of powder taken. The sedimentation curves are similar for the various charges, each of these latter corresponding to its own "saturation resistance" (for 0.75 g, 3.5 Ω; for 1 g, 2.5Ω; for 3 g, 0.8 Ω and for 15 g, 0.4 Ω).

The influence of oxygen, acetylene and methylethylacetyleneylcarbonyl on the resistance of 0.75 g of Raney nickel saturated with hydrogen was studied at 20°. In all cases the use of these substances for removing hydrogen from the catalyst surface led to an increase in the resistance. By passing a current of acetylene through a suspension of Raney nickel in n-heptane, the resistance of the catalyst sharply increases, reaching 1 million ohms in the course of 15-20 minutes and then remaining at this level. On displacing the acetylene in the gas phase with hydrogen, and hydrogenating the adsorbed acetylene and the products of its partial polymerization, the hydrogen is taken up at a high rate and is initially without effect on the conductivity of the powder (see Fig.2, A, a). Only after the solution has bleached is there observed a sharp decrease in the rate of hydrogen take-up and, at the same time, a pronounced increase in the conductivity of the powder. The "saturation resistance" is established approximately 30 minutes after the beginning of hydrogenation.

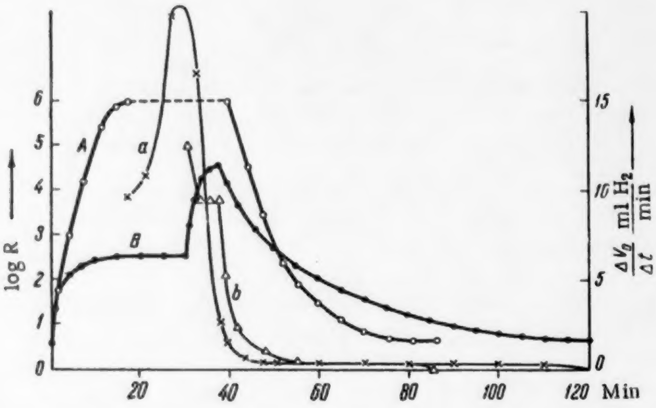

Fig. 2. The variation in the resistance of Raney nickel due to hydrogenation of acetylene (A) and of methylethylacetyleneylcarbonyl (B). Kinetic curves for acetylene (a) and for the carbonyl (b).

On agitating the powder in air, the resistance also reaches one million ohms; if the contact with air was brief, the basic mass of the powder on saturation with hydrogen takes up the latter at a resistance of 1 M Ω and the remaining, smaller portion, at the "saturation resistance." The entire process of saturation extends over several minutes. After prolonged contact with oxygen, subsequent saturation with hydrogen stretches out over 2-3 hours and the basic part of the hydrogen is taken up at the "saturation resistance" (Fig. 2, B, b).

On introducing methylethylacetyleneylcarbonyl in an atmosphere of nitrogen into the hydrogenation flask, the resistance of the powder falls and reaches a constant value, corresponding to the fraction of hydrogen which has been removed. With subsequent hydrogenation, the resistance again increases somewhat during an intensive take-up of the hydrogen, and then sharply falls. Hydrogenation of the carbonyl at the expense of the hydrogen of the gaseous phase also leads to a marked rise in the resistance of the powder, the hydrogen being taken up with considerable velocity. It is characteristic of the Raney nickel that the jump in resistance from 10 to 1,000,000 Ω occurs on removing only 15% of the adsorbed hydrogen (18 ml H_2 per 1 g of Raney nickel).

It is clear that it is the hydrogen which is adsorbed on the surface (possibly in molecular form) which determines the mechanism of high conductivity in the nickel powder. Its amount as determined by the method of electrical conductivity, is in good agreement with the data from potentiometric measurements [2]. In a hydrogenation on Raney nickel, practically all of the resistance is observed in the region corresponding to the removal of more than 15% of the hydrogen. Cyclohexane is an exception. Similar results were obtained with platinum black. In distinction to nickel, however, oxygen here increases the resistance only up to 2000Ω.

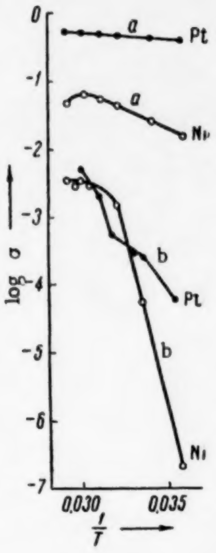

Fig. 3. The relation between the temperature and the electrical conductivity of Raney nickel and platinum black. a) powder, saturated with hydrogen; b) hydrogen partially removed from the powder surface.

As is to be seen from Fig. 3, with an increase in temperature the conductivity of the Ni' and Pt powders increases linearly in the coordinates log σ vs 1/T, but the absolute magnitude of this change depends on the nature of the substance which has been adsorbed on the surface. In the case of nickel, the conductivity begins to fall after 50°; for platinum it is increasing even above 70°.

The temperature curves for the electrical conductivity of Raney nickel and platinum black show the form which is characteristic for semiconductors [3]. The slope of their linear portion permits the calculation of the dissociation energy of the current carriers. In the cases of Raney nickel and platinum black, this energy proves to be very close to the energy of activation of hydrogen and the unsaturated compounds on these catalysts. For Raney nickel in n-heptane, the dissociation energy of the current carriers is equal to 1200 cal/mole when the surface is covered with hydrogen, but when the hydrogen is displaced from the surface by an unsaturated compound it rises to 9000 cal/mole.

If account is taken of the fact that with Raney nickel a negative temperature coefficient is frequently observed in the hydrogenation reaction after 45-50° and that for platinum such a coefficient is characteristic of temperatures above 100°, it is possible to reach certain conclusions concerning the relationship between the conductivity of these substances and their catalytic activity. Here at least the surface layers, if not the entire mass of the catalytic particles, show the properties of semiconductors. The hydrogen or unsaturated compounds which are adsorbed on the powder surface can play the role of surface additives, the absolute magnitude of the conductivity of the catalyst depending on their donor or acceptor properties [3].

It should be noted that the specific conductivity of these powders, when calculated for a layer 6 cm × 1 mm, has a value of the order of 10^{-2} $\mathrm{ohm}^{-1}\cdot\mathrm{cm}^{-1}$ in the case of the adsorption of hydrogen and diminishes by 6 orders in the adsorption of an unsaturated compound, as is characteristic of the semiconductors. The method which has been proposed is distinguished by a high sensitivity; it renders possible judgments as to the concentrations of reacting substances on catalyst surfaces and permits a study of the laws applying to the adsorption of unsaturated compounds. With this method it has been shown that the change in the electrical conductivity of powdered metals is related to their catalytic activity and is that which is characteristic of semiconductors.

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CONCERNING THE POSSIBILITY OF THE LIQUID PHASE OXIDATION OF BENZENE TO PHENOL

N. M. Emanuel and E. T. Denisov

(Presented by Academician N. N. Semenov May 15, 1957)

Recently the question has been raised by one of us [1] as to the expediency of carrying various high temperature gaseous phase oxidations over into low temperature oxidations in the liquid state by using the principle of gaseous initiation for reaction stimulation.

The effectiveness of this proposal was illustrated by the example of the oxidation of compressed n-butane at temperatures close to the critical. In many other processes, the extensive destructive oxidation which is characteristic of high temperature reactions in the gaseous phase is also a fundamental impediment to the formation of valuable oxygen-containing products through direct oxidation. Among such processes there should unquestionably be listed the oxidation of benzene to phenol. Benzene is one of the most difficultly oxidizable hydrocarbons. The resistance of benzene to oxidation by molecular oxygen is in the first instance to be related to the high stability of the C-H bonds in the molecules of the compound (102 kcal/mole). In the gaseous phase, oxidation proceeds with considerable velocity even at temperatures of 600-700°. In addition to small quantities of phenol, tars and very large amounts of the products of deep combustion, CO, CO_2 and water [2, 3], are also formed.

A similar situation is also met in the gaseous phase oxidation of n-butane. For carrying out this process there is required a temperature of about 400°, at which an extensive and useless combustion of the hydrocarbon is also observed. This state of affairs is essentially altered in carrying out the oxidation of compressed butane. In this case the process develops even at 130-150° with the exclusive formation of acetic acid and methylethylketone, products of "soft" oxidation.

It was reasonable to hope that positive results might come from an attempt at carrying out of the oxidation of benzene in the liquid phase at temperatures close to the critical. Since for benzene $t_{cr} = 288°$ and $p_{cr} = 48$ at., we attempted to observe the oxidation of this substance at temperatures of 230-270° under a pressure of 50 at.

These experiments were carried out in the autoclave apparatus which is used for the gaseous phase oxidation of hydrocarbons under pressure. In each experiment the reactor was loaded with 200 ml of benzene. Oxidation was carried out by the oxygen of a 1 : 1 nitrogen-oxygen mixture at a flow velocity of 20 liter/hr. During the process, samples of the oxidized benzene were removed and analyzed for phenol. With the aid of a photocolorimeter the optical density of the oxidized benzene was also measured, this factor characterizing the production of tars.

The experiments showed that in the liquid phase the oxidization of benzene proceeds with measurable speed at 250°. Phenol and tars were formed in this oxidation. The kinetic curve for the formation of phenol was S-shaped. The maximum concentration of phenol in this process is not great, however, and amounts to only 0.16 mole%. The kinetic curve for the formation of phenol in this experiment is shown in Fig. 1 (Curve 3).

An experiment with cobalt stearate as a catalyst, led to an unexpected result. It is known that this catalyst accelerates the oxidation of many hydrocarbons. The 250° oxidation of benzene with cobalt stearate showed, however, that the catalyst in this instance directs the reaction toward the condensation of benzene, graphite being formed and phenol produced in small amounts. The maximum concentration of the phenol resulting from oxidation with cobalt stearate is 0.11 mole %, i. e., it is less than that in the uncatalyzed oxidation (Fig. 1, Curve 1).

Experiments on the oxidation of benzene in the presence of small amounts of such easily oxidizable substances as cyclohexane and cyclohexanone, showed the acceleration action of these materials on the oxidation. These are competitive oxidizations of two materials, the easily oxidizable substance initiating the oxidation of benzene. In Fig. 2 there are shown kinetic curves for the formation of phenol and adipic acid in the oxidation of benzene with 1 mole % added cyclohexanone. In this case a considerably higher maximum phenol concentration, amounting to 0.5 mole %, is reached. The kinetic curves for the formation of phenol and adipic acid run practically in parallel and retardation in the formation of the two products occurs simultaneously.

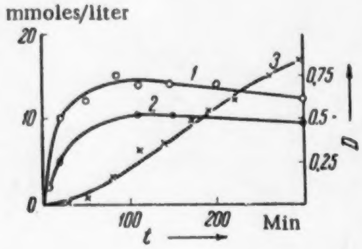

Fig. 1. The oxidation of benzene at 250° in the presence of 0.15 mole % St_2Co and 2% cyclohexane. 1) The kinetic curve for the formation of phenol; 2) the variation of optical density; 3) the kinetic curve for the formation of phenol in an experiment without a catalyst at 250°.

It is interesting to note that the "damping" of this process is not related to the consumption of the added inductor (at the end of the reaction there remains 0.3 mole % of unreactive cyclohexanone), but to the self-retardation of the reaction by the oxidation products from the benzene. The best yield of phenol was obtained in experiments with nitrogen tetroxide as a gaseous initiator. In these experiments, air which had been enriched with oxygen was, prior to introduction into the reactor, passed through a trap with liquid nitrogen tetroxide where it was saturated with NO_2. The concentration of the NO_2 amounted to 2% by volume.

In Fig. 3 there are shown kinetic curves for the formation of phenol during the oxidation of benzene in experiments without an initiator at 250° (Curve 3) and in experiments with an initiator at various temperatures (Curves 1 and 2). It is to be seen from the figure that the application of a gaseous initiator makes it possible to accelerate the formation of phenol and to raise its maximum concentration from 0.16 to 0.8% at 250° and to 1.1% at 267°. In addition to the phenol, the formation of nitrobenzene was also noted in the experiments with the gaseous initiator.

The data which have been obtained on the oxidation of benzene indicate that this is a degenerate-branching [4], self-retarding chain reaction. The kinetic data are in good agreement with the following mechanism. In the reaction, the generation of chains results from initiator action, at a velocity w_0 and from degenerate branching at an intermediate product P, at a velocity $k_3[P]$. Chain rupture at a velocity k_4n^2 occurs because of recombination of the free radicals. According to the method of stationary concentrations, the total concentration of the free radicals is equal to $n = \sqrt{\frac{w_0 + k_3[P]}{k_4}}$.

Let the intermediate product be converted by a chain to a final product K. This final product by reacting with the radicals, leads to a replacement of part of the active radicals by less active ones, which are capable of interacting with the intermediate product but do not react with the initial hydrocarbon. The analysis of such a system gives the following differential equations (in dimensionless variables) for the rates of formation of the intermediate and the final products

$$\frac{d\pi}{d\tau} = \frac{\omega_0 + \pi}{\sqrt{\omega_0 + \pi} + \alpha\xi} - \pi\sqrt{\omega_0 + \pi}$$

$$\frac{d\xi}{d\tau} = \pi\sqrt{\omega_0 + \pi},$$

where

$$\pi = \frac{[P]}{p_{max}}; \; p_{max} = \frac{k_1[RH]}{k_2}; \; \xi = \frac{[K]}{p_{max}};$$

$$\omega_0 = \frac{w_0}{k_3 p_{max}}; \; \tau = k_2\sqrt{\frac{k_3 p_{max}}{k_4}}\,t; \; \alpha = \frac{k_5 p_{max}}{k_4}$$

k_1 is the velocity constant for the reaction of the active radicals with the hydrocarbon; k_2 is the velocity constant for the reaction of the radicals with the intermediate product and k_3 is the velocity constant for the reaction of the radicals with the final product.

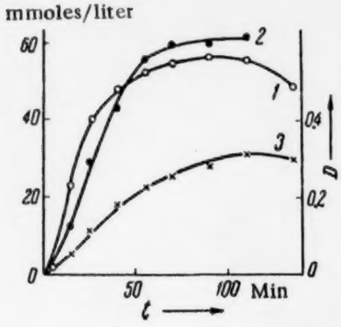

Fig. 2. Kinetic curves for the formation of phenol (1), and dicarboxylic acid (2) from cyclohexanone and for the variation of the optical density of the reacting mixture during 250° oxidation of benzene with 1 mole % added cyclohexanone (3).

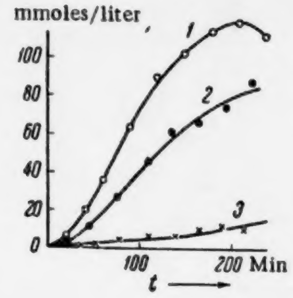

Fig. 3. Kinetic curves for the formation of phenol in experiments on the oxidation of benzene with continuous gaseous initiation by nitrogen tetroxide at various temperatures: 1) 267°; 2) 250°; 3) kinetic curves for the formation of phenol at 250° in an experiment without initiation.

In the first equation the term $\frac{\omega_0 + \pi}{\sqrt{\omega_0 + \pi + \alpha\xi}}$ covers the rate of formation of the intermediate product resulting from the reaction of the active radicals with the hydrocarbon. It is clear that in the course of the reaction this velocity diminishes as the concentration of the final product increases. The term $\pi\sqrt{\omega_0 + \pi}$ characterizes the consumption of the intermediate product. Obviously the maximum concentration of this intermediate product is the greater, the greater the rate of chain initiation, ω_0. If $w_0 \gg k_3[P]$ and thus $\omega_0 \gg \pi$, so that $\sqrt{\omega_0 + \pi} \approx \sqrt{\omega_0}$, then $\pi_{\max} = \frac{\sqrt{\omega_0}}{\sqrt{\omega_0} + \alpha\xi}$. Such a qualitative relation has also been obtained by us in experiments with a gaseous initiator, the application of which permits the maximum concentration of phenol to be increased several fold. The kinetic curves π, which have been constructed by graphical integration of our system of two differential equations, are S-shaped with clearly expressed maxima. In our experiments the kinetic curves for the formation of phenol are of exactly this same type.

Thus the present investigation has shown the possibility in principle of the liquid phase oxidation of benzene to phenol at temperatures close to the critical with the application of that principle of gaseous initiation which gives the best results. At the same time the perspectives for further investigations become clear: it is necessary to seek means for removing the effects of self-retardation.

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DETERMINATION OF THE IRON VAPOR PRESSURE OVER AUSTENITE

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(Presented by Academician G. V. Kurdyumov. May 22, 1956)

The iron–carbon system, which has important practical significance, was submitted to numerous thermodynamic investigations. These investigations were followed by the very precise work of Smith [1] who made a study of the equilibrium between the carbon dissolved in the metal and the gaseous mixture CO–CO_2 and CH_4–H_2. All the experiments showed that the heat of solution of carbon in γ-iron is independent of the concentration of carbon and is approximately equal to 10 kcal/g-atom. It was demonstrated that the solutions of carbon in γ-iron show significant deviations from the law of ideal solutions of solids: the activity of carbon increases with the concentration more rapidly than a linear function will warrant.

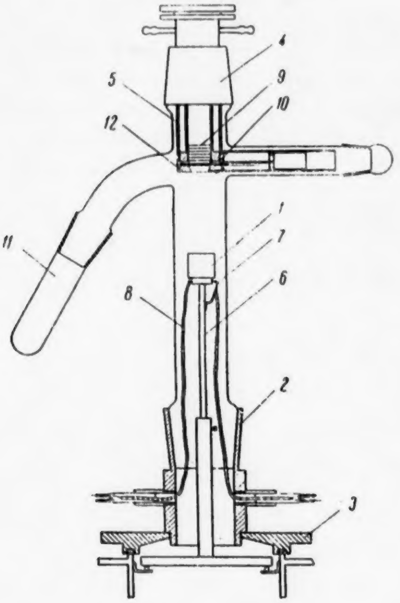

Fig. 1. Diagram of the apparatus: 1) Knudsen's flask (made of tantalum); 2) lower cross section; 3) flange of the evacuating system; 4) cross section of the condensing system; 5) refrigerator; 6) support for the Knudsen flask; 7) regulating thermocouple; 8) measuring thermocouple; 9) targets; 10) screen; 11) collector of the products of target exposure; 12) collimator.

The causes of the nonideal behavior of γ-iron solutions of carbon are discussed in another publication [2]. Assuming that the partial heat content of the components is independent of the concentration, and taking into consideration the specificity of the solid solution of the inclusions, the authors derive an equation for the activity coefficient of carbon in austenite, an equation which agrees with the experimental results obtained by Smith [1].

The investigation of the thermodynamic properties of austenite were studied by measuring the vapor pressure, using the Knudsen method [3]. In this work, the heats of sublimation for pure iron and for iron alloys with carbon were determined on the basis of the effect of temperature on the iron vapor pressure. The heat of sublimation was found to be: 103.5 kcal/g-atom for pure iron, 54.6 kcal/g-atom for an austenite containing 4.5 atom % C and 43.5 kcal/g-atom for an austenite containing 5.8 atom % C. The results of these experiments led to the conclusion that the heat of dilution of iron ΔH_{Fe} is very strongly affected by the concentration of carbon: when the concentration of carbon is 4.5 atom % it is equal to + 48.9 kcal/g-atom, while when carbon concentration is 5.8 atom %, ΔH_{Fe} = + 60 kcal/g-atom. Yet, according to Smith [1] the heat of dilution of carbon in austenite is independent of the concentration.

Thus, the results of Smith [1] and Kornev [3] are contradictory and do not satisfy the Gibbs-Duheme equation:

$$x_{Fe} \frac{\partial \Delta \overline{H}_{Fe}}{\partial x_{Fe}} = x_C \frac{\partial \Delta \overline{H}_C}{\partial x_C}. \qquad (1)$$

It must be noted that Smith's results were partially confirmed by Müller [4] who studied the equilibrium reaction between carbon dissolved in austenite and the gaseous mixture $CO-CO_2$.

The present work concerns the determination of the thermodynamic characteristics of austenite; it was undertaken in order to check the results obtained by Kornev [3] and to increase their precision.

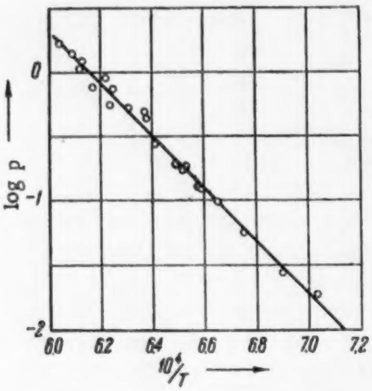

Fig. 2. Effect of temperature on the vapor pressure of iron.

We have determined the vapor pressure of iron on austenite by the Knudsen method using the radioactive isotope Fe^{59}. The plan of the apparatus used is presented in Fig. 1.*

We have investigated pure iron and its alloys with 2.7 and 4.3 at. % C within the temperature range 1150° to 1350°. Electrolytic iron, activated in a physical reactor, was used for the preparation of samples. The alloys were prepared by smelting pure iron with synthetic cast iron in a helium atmosphere. Since no burning of carbon occurred, the composition of the alloy was determined according to the data of blast furnace mixtures.

The results of the experiments are presented in Figs. 2 and 3, where each experimental point corresponds to the average value of 2 or 3 measurements. It must be noted that all the experiments were made in such a way that the first measurements corresponded to lowest temperatures. Figure 3 shows that at low temperatures the experimental points do not fall on a straight line but are somewhat higher. Furthermore, the values of vapor pressure determined at low temperatures are not reproducible; they have a tendency to decrease. In Fig. 3, A, the points corresponding to low temperatures are averages of 3 measurements (each measurement took one hour) which may differ by as much as 80%. Taking all these conditions into account, it is natural to assume that at low temperatures the samples are in a nonequilibrium condition.

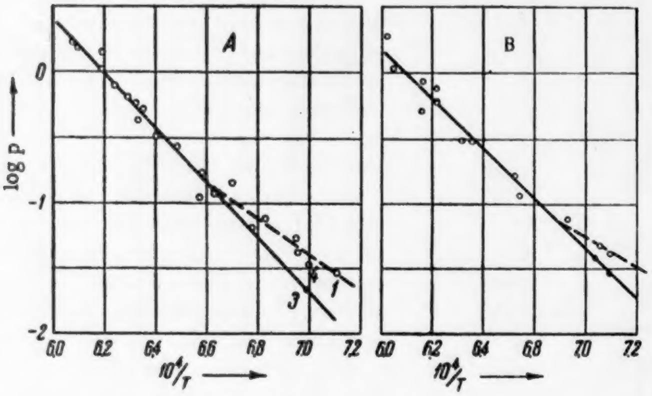

Fig. 3. Effect of temperature on the vapor pressure of iron over austenite. A) 2.7 atom % C; B) 4.3 atom % C.

It is known that in iron and in its alloys, because of the $\alpha \longrightarrow \gamma$ transformation, a recrystallization takes place as a result of which the grains of the metal undergo phase cold hardening. The free energy of these grains becomes somewhat higher. This statement is borne out by the fact that as the temperature increases the austenite undergoes recrystallization during which the grains with distorted crystal lattices are replaced by very small grains with a regular lattice. All this should lead to a certain increase of vapor pressure at temperatures slightly exceeding the recrystallization temperature.

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* A more detailed description of the method used can be found elsewhere [6].

In order to check this hypothesis we performed the following experiments. After measurements at low temperatures (Fig. 3, A, point 1), the sample was subjected to a temperature of 1300° (point 2) then measurements were performed again at low temperature (point 3); the last point fell directly on the straight line. After this, without destroying the vacuum, the sample was cooled down to room temperature and the measurements were performed again (point 4); Figure 3, A shows that point 4 does not fall on the straight line. Thus the low temperature points which fall above the straight line correspond to the thermodynamically nonequilibrium condition of austenite and should not be taken into account. It is interesting that no such effect takes place for pure iron. This can be explained by the fact that in pure iron the effect is so small that the precision of the experiment was insufficient to allow its detection.

The results obtained for pure iron allow us to express the vapor pressure (in dynes/cm^2) as the function of temperature in the following way:

$$\log p = -\frac{20630}{T} + 12.70 \tag{2}$$

One must note that the results concerning pure iron differ somewhat from those obtained by Kornev [3] but are in agreement with the results obtained by Edwards [5].

Heats of sublimation calculated on the basis of the results obtained are as follows: 94.5 kcal/g-atom for pure iron, 95.0 kcal/g-atom for the alloys with 2.7 at.% C, 89.3 kcal/g-atom for the alloys containing 4.3 at.% C.

Thus the heat of sublimation is almost independent of the concentration of carbon. This result is in good agreement with the results published by Smith [1]. The dependence of heat of sublimation on carbon concentration found by Kornev is apparently due to the fact that in his experiments the measurements were made at temperatures lower than those used in our experiments. Our experiments show that at low temperatures the vapor pressures measured correspond to nonequilibrium condition of austenite undergoing a transformation during the experiment.

The author is deeply grateful to G. V. Kurdyumov, Member of the Academy, and L. A. Shvartsman, Doctor of Chemical Sciences, for the attention they gave to our work and also for their valuable advice.

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THE QUESTION OF THE ACTION OF COMPLEX CATALYSTS FOR THE POLYMERIZATION OF VINYL COMPOUNDS

A. A. Korotkov and L. B. Trukhmanov

(Presented by Academician V. A. Kargin May 23, 1957)

There is a divergence of opinion as to the nature of the catalytic activity of those newly discovered [1-4] complex catalysts of indefinite composition which are obtained as products of the interaction between the halides of the transition metals of Groups 4, 5 and 6 in the Periodic System and the alkyls of the metals of Groups 1, 2 and 3.

In analogy with his ideas on the mechanism of polymerization of the alkali-organic compounds [5], Ziegler [1] considers the reaction here to have a multistage mechanism, in each stage of which there is an addition of one molecule of the monomer of a stable metalloorganic compound. He rejects the possibility that the reaction might proceed with the participation of free radicals or according to a mechanism of acid catalysts. Natta [4, 6] favors a mechanism of alkaline catalysis with the carbon ions as active centers. Finally, Nenitzescu [7] has advanced arguments in support of a free radical reaction.

A suitable method for fixing the class of any new polymerization catalyst is that based on the determination of the composition of the copolymer which results from the copolymerization of two monomers of different polarities [8]. The styrol-methylmethacrylate monomer pair is most characteristic here, since, depending on the reaction mechanism, the resulting copolymers are sharply distinguished from one another in composition [9]. But over a wide interval of temperatures (from −80° to 60°) neither methylmethacrylate nor acrylonitrile are polymerized by the complex catalysts, even when the latter are in excess (up to 10% of catalyst per mass of monomer has been investigated). Polymerization also fails to occur in equimolar mixtures of styrol and methylmethacrylate or acrylonitrile.*

For this reason we have studied the monomer pair styrol– 7 α-methylstyrol. Toluol served as the solvent in all experiments; the ratio of the monomers was close to that of an equimolar mixture at total concentrations of from 1.7 to 2.5 g moles/liter. As catalysts there were employed: ethyl lithium, triethyl aluminum, titanium tetrachloride and a complex which was the product of the interaction of the last two. Polymerization was carried out in ampules which were divided by a partition: in the one section there was introduced the solution of the monomers in toluol; in the other, the solution of the catalyst. After filling and sealing, the ampules were held at room temperature for from one-half hour to several hours. Reaction proceeded almost instantaneously in mixing the solutions of titanium tetrachloride and triethyl aluminum, a black precipitate being formed. The ampules were placed in a thermostat and after their contents had come to the bath temperature, the partition was ruptured and the two solutions mixed. In order to halt the reaction, the ampules were broken, their contents run into methyl alcohol and the polymer carefully washed with the latter.

The number of α-methylstyrol units in the precipitated copolymer was determined by infrared spectroscopy of the 1111 cm^{-1} adsorption band. The precision of measurement amounted to ± 5% of the measured value.** The principal conditions and the results of the experiments are presented in Tables 1 and 2.

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* Our results are in complete agreement with the data of Kolesnikov [12], who also failed to obtain acrylonitrile polymers with complex catalysts.

** These measurements were carried out by E. I. Pokrovsky.

TABLE 1

Experiment No.	Catalyst	Initial concentration (g moles / l)				Duration of experiment (min)	Temperature of polymerization (°C)	Degree of polymerization (%)	Proportion of α-methylstyrol units in copolymer (mole %)
		catalyst (1 component)	triethylaluminum	styrol	α-methylstyrol				
67	Ethyl lithium	0.023	—	1.07	1.37	5	20	21	0
70		0.054	—	0.87	0.87	900	−20	17	0
64		0.041	—	0.96	1.05	1080	20	52	2
65		0.065	—	1.01	1.10	14	20	49	3
66	Titanium tetrachloride	0.0037	—	1.00	1.09	1	−80	13	70
51		0.0121	—	1.00	1.08	3	−80	43	69
68	Titanium tetrachloride + triethyl aluminum	0.009	0.010	0.93	1.01	3	−80	24	70
42		0.016	0.011	0.98	1.07	270	−80	36	77
53		0.011	0.007	0.85	0.92	85	−80	39	57

TABLE 2

Experiment No.	Number of moles of triethyl aluminum per 1 mole of titanium tetrachloride	Initial concentration (gmoles/l)				Duration of polymerization (hours)	Temperature of polymerization (°C)	Degree of polymerization (%)	Proportion of α-methylstyrol units in copolymer (mole %)
		triethyl aluminum	titanium tetrachloride	styrol	α-methyl styrol				
44	0.7	0.017	0.012	0.95	1.03	1	−80	1.6	68
58	1.1	0.019	0.021	0.94	1.02	0.2	−80	3.2	76
54	1.7	0.013	0.021	1.01	1.05	1.6	−80	2.9	69
57	3.2	0.018	0.057	0.87	0.87	18	−80	2.1	74

The pure monomers were polymerized by three of the investigated catalysts and were not polymerized by triethyl aluminum. The polymerization of α-methylstyrol by ethyl lithium proceeds slowly: after 20 hours at 18°, 38% of the monomer had reacted.

For chain radical copolymerization of styrol and α-methylstyrol, the copolymerization constants are respectively $r_1 = 0.71$ and $r_2 = 0.14$ [10]. Thus the copolymer which is formed in the initial stage of the copolymerization of an equimolar mixture of these monomers should contain 60 styrol units and 40 α-metastyrol.

On the basis of the compositions of the resulting copolymers (see Table 1), the complex catalysts should be classed among the acid catalysts. Naturally, their acidic properties do not alter with the ratio between the initial components of the catalyst (see Table 2).

For the assignment of the complex catalysts to the acid class it should also be noted that the polymerization of methylmethacrylate and acrylonitrile does not take place in their presence, whereas with butyl lithium and other alkaline catalysts it is possible to obtain polymers of high molecular weight, even at temperatures considerably below zero [11].

The difference between the complex and the acid catalysts is not to be sought in the nature of the active centers which are responsible for the growth of the polymer chain, as has been done by Natta [6], but in the structural peculiarities of the heterogeneous catalysts.

Because of peculiarities in the crystal structures, it is very likely that in the case of the complex catalysts the adsorbed monomer molecules react with the active centers on the catalyst surface. It is natural that the rate of polymerization should prove to be low for those compounds such as isobutylene, pseudobutylene, etc. which adsorb to a very small extent on the catalyst surface. On the other hand, the molecules of the simplest unsaturated hydrocarbons (ethylene, propylene, primary butylene) are activated by adsorption and in this active condition prove to be capable of reacting at high velocity with the active centers on the same catalyst surface. With the ordinary acid catalysts (aluminum chloride, boron fluoride, etc.) the rate of polymerization of the indicated monomers is low because of the lack of preliminary activation, and the polymers which result have low molecular weight.

This hypothesis explains all of the principal observations of Ziegler, Natta and ourselves on polymerization by complex catalysts. For example, it follows from this hypothesis that, on passing in the complex catalysts from triethyl aluminum to triisobutyl aluminum or from ethyl lithium to isobutyl lithium there should be a pronounced change in the rate of the chain initiation and, as a result, in the overall reaction velocity. In polymerization in solutions of hydrocarbons such as toluol, which have pseudoacidic properties, the reaction of chain transfer which is observed during polymerization with basic catalyst does not have essential significance. These hypotheses and certain others will serve as objects of our further investigations.

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THE OXIDATION OF CUMENE BY MOLECULAR OXYGEN IN EMULSIONS CONTAINING VARIOUS EMULSIFIERS

R. V. Kucher, A. I. Yurzhenko and M. A. Kovbuz

(Presented by Academician P. A. Rebinder. May 21, 1957)

The chain theory of the oxidation of hydrocarbons which was developed from experimental data by N. N. Semenov [1] has been taken up by a number of investigators. In the papers of N. M. Emanuel and his coworkers [2] the kinetic aspects of the liquid phase oxidation of hydrocarbons have been studied for the process as carried out in a homogeneous phase in the presence of various catalysts. The work of [3] has been devoted to the liquid phase oxidation of cumene and the influence of various additives (initiators and inhibitors) on it.

The presence of an aqueous alkaline solution exerts a material influence on the rate of oxidation of hydrocarbons [4]; from our point of view much interest attaches to the role of such an aqueous phase (and its composition) as a kinetic factor and yet data concerning its effect on the kinetics of hydrocarbon oxidation is very limited and unsystematic.

The study of the emulsion oxidation of hydrocarbons is of general interest in connection with the mechanism of reactions in emulsions; in particular, it is of interest in its relation to the topochemistry and mechanism of oxidation processes in emulsion systems. The kinetics of this process can be effected by the phase ratio, by the electrolyte composition of the aqueous phase and by the specific properties (micellular structure, conjugate solubility of the original hydrocarbon and the resulting peroxides, stabilization of the emulsion, etc.) of the colloidal electrolytes (emulsifiers) which may be present. In view of the technical ease of controlling these processes, a knowledge of the mechanism of the reactions of hydrocarbon oxidation in emulsions would also open perspectives for their industrial application. Finally, the formation and breakdown of hydroperoxides in emulsions are of great significance for the emulsion polymerization of unsaturated compounds, the peroxides in this case being the initiators of the reaction.

It was the purpose of the present work to study the rate of oxidation of cumene in emulsions containing various emulsifiers and its relation to the phase ratio and the nature of the emulsifier.

The oxidation of the purified [3] hydrocarbon was carried out in glass flasks thermostated at 80°, through which pure oxygen was bubbled (the discharge of the latter was controlled rheometrically). At definite intervals of time, samples were taken from the reaction mixture (the hydrocarbon and the aqueous phases separately) and analyzed for the hydroperoxide [5]. The cumene phase was, in addition, analyzed for the total yield of carbonyl compounds [6]. In all cases the rate of introduction of O_2 was constant and equal to 20 ml/min. 0.1 g equiv/liter of Na_2CO_3 was maintained in the aqueous phase, this leading to pH 9.9.

In Figure 1 there are shown kinetic curves for the yield of cumene hydroperoxide in the absence of emulsifiers at various phase ratios. From these data it follows that an increase in the volume of the aqueous phase markedly increases the rate of production of the cumene hydroperoxide. These data have been confirmed in other systems and indicate that the aqueous phase is an essential kinetic factor in the oxidation of hydrocarbons in emulsion, it being the zone where the process is initiated and the hydroperoxide formed. As experiment shows, the significance of the aqueous phase in the emulsion oxidation of cumene is particularly enhanced by the presence of colloidal electrolytes (emulsifiers) which contain surface active anions. In Fig. 2 there are presented kinetic curves for the production of cumene hydroperoxide in the presence of various emulsifiers. It is to be seen from these data that under fixed and uniform conditions, the emulsifiers accelerate the formation of the hydroperoxide. In this case the role of the emulsifier cannot be reduced to that of a simple stabilizer of the emulsion since a variation in the nature of the emulsifier only slightly alters the degree of dispersion of the emulsion, whereas the rate of formation of the cumene hydroperoxide changes markedly.

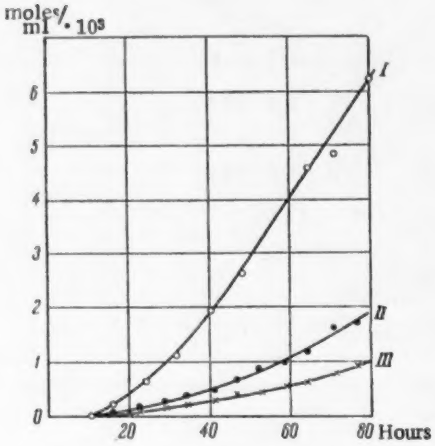

Fig. 1. Kinetic curves for the yield of cumene hydroperoxide at various phase ratios (cumene: aqueous phase) in the absence of emulsifiers. I) 1 : 4, II) 1 : 1; III) in the absence of an aqueous phase.

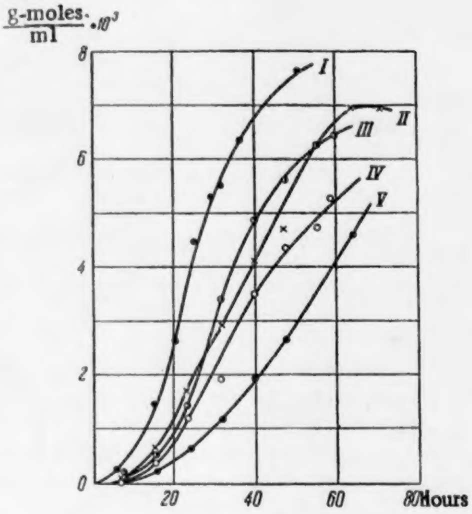

Fig. 2. Curves for the yield of cumene hydroperoxide in the presence of emulsifiers (phase ratio 1 : 4) I) 2% K palmitate; II) 2% aerosol OT; III) 2% Na caprylate; IV) 2% leucanol; V) in the absence of an emulsifier.

We also note that in the initial stages of the reaction, the absorbed oxygen is consumed practically completely in the formation of the hydroperoxide. The amount of oxygen converted into the hydroperoxide is somewhat diminished (to 90%) after the accumulation of 15-20% of the cumene hydroperoxide. In the presence of emulsifiers (aerosol OT, potassium palmitate) the final yield of the hydroperoxide amounts to about 95% of the cumene oxidized, this being considerably greater than the yield of cumene hydroperoxide obtained by homogeneous oxidation in the condensed phase (50%). During oxidation in the presence of emulsifiers a change in the stability of the emulsion is also noted; in the course of the first 16-20 hours the cumene emulsion is stable, prolonged centrifuging being needed for the separation of the phases; beyond this the emulsion becomes considerably less stable and rapidly separates into layers.

The data which have been obtained permit the conclusion that it is principally in the aqueous phase that reaction is initiated and the hydroperoxide formed during emulsion oxidation of the hydrocarbon. The initial formation of the hydroperoxide in the aqueous phase is, first of all, the result of an increased absorption of the oxygen in the presence of the emulsifier or colloidal electrolyte. As we have shown in supplementary experiments, the solubility of the oxygen in this case increases several fold. In the aqueous phase there is also found conjugately dissolved cumene. Because of the increased absorption of O_2, this part of the hydrocarbon is under conditions which are especially favorable for oxidation. The development of the reaction chain can be represented by the equations

$$\dot{R} + O_2 \rightarrow RO\dot{O}; \quad RO\dot{O} + RH \rightarrow ROOH + \dot{R}.$$

The initiation of these processes involves the formation of free hydrocarbon radicals, $\dot{R}$. These latter can be generated through the purely thermal decomposition of the product hydroperoxide according to the reactions

$$ROOH \rightarrow R\dot{O} + \dot{O}H; \quad R\dot{O} + RH \rightarrow ROH + \dot{R}.$$

This decomposition of the peroxide proceeds at a much higher velocity in the aqueous alkaline medium than it does in the hydrocarbon. Not only the hydroxyl ions, but also the emulsifiers exert an influence (accelerating or retarding) on the thermal breakdown of the peroxide (Table 1).

TABLE 1

The Solubility and Velocity Constants for the Breakdown of Cumene Hydroperoxide in Aqueous Solutions of Emulsifiers

Medium	Solubility of CHP, in % at 20°	$k \cdot 10^3$ at 98.5°
Water	1.46	0.183
0.1 N Na_2CO_3 solution	1.38	1.57
2% aerosol OT	3.39	1.27
2% Na caprylate	1.61	2.08
2% K palmitate	4.87	1.96
2% leucanol	1.98	1.83
Cumene	∞	0.242

In addition to the specific effect of the emulsifier on the breakdown of the cumene hydroperoxide, it is also necessary to take account of the conjugate solubility of the hydroperoxide in the aqueous phase. An increase in the concentration of cumene hydroperoxide in the aqueous phase aids the generation of free radicals. The accumulation of the hydroperoxide in the aqueous phase can, however, proceed only so far, since it is limited by the solubility. With a further increase in the amount of the hydroperoxide in the reaction mixture, it passes into the hydrocarbon phase, where its breakdown proceeds to a considerably smaller degree. Thus the hydrocarbon phase is a special type of "depot" for the hydroperoxide. It is in this connection that there is to be understood the decrease in the emulsion stability in the course of the process. Because of its surface activity, the hydroperoxide is adsorbed on the phase interface when its concentration in the hydrocarbon becomes pronounced, the mechanical strength of the adsorbed layer of emulsifier being thereby diminished and its stabilizing action consequently reduced. Such a "storing" of the cumene hydroperoxide in the hydrocarbon phase can also explain the increased yield of the hydroperoxide during cumene oxidation.

Thus, the emulsion oxidation of cumene by free oxygen is accelerated because its basic stages (the initiation and development of the hydroperoxide formation) proceed in the aqueous phase, the emulsifying agent playing an essential and specific role. This latter makes it possible to increase the yield of the hydroperoxide and to facilitate the control of the process.

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A MASS SPECTROSCOPIC INVESTIGATION OF THE PRODUCTS OF DISCHARGE IN WATER VAPORS

G. K. Lavrovskaya, V. E. Skurat, V. L. Talroze and
G. D. Tantsyrev

(Presented by Academician V. N. Kondratyev. May 16, 1957)

The experimental investigation of the free radicals and atoms which are extracted in a jet from the glow discharge in water vapors has been dealt with in a number of papers [1-4]. This is a fundamental problem since the discharge in water vapors is employed as a source of active particles in studies of the reactions of the latter [3]; in addition a knowledge of the composition of the discharge products is necessary for understanding the mechanism of the discharge reactions and, possibly, of radiochemical reactions as well.

Free hydroxyl radicals have been spectroscopically detected [1, 2] in the discharge products in water vapors, their concentration having been determined with satisfactory precision. Direct spectroscopic measurements of atomic hydrogen have not been carried out, although in the older papers [5] there are certain indications as to the possibility of its formation. At the same time oxygen atoms at concentrations considerably exceeding those of the free hydroxyls under the experimental conditions have been detected by L. I. Avramenko [3] from the luminescence on addition of NO and from a number of chemical characteristics.

It is thus of interest to carry out mass spectrometric measurements on the atoms and radicals which are formed by discharge in water vapors, and this has been done in the present work.

These measurements have been performed with a mass spectrometer which was specially designed for the determination of free radicals and atoms.* A special feature of this apparatus was the introduction of a molecular beam of the analyzed material into the ion source. By periodically interrupting this beam with a shutter and measuring only that component of the lines of the mass spectrum which is thereby altered ("modulated"), it was possible to shut out the "background" of the apparatus and to avoid, in a considerable measure, that suppression of the spectra of the free radicals and atoms which results in a mass spectrometer of the usual type because of their heterogeneous loss on the walls of the ionization chamber. This latter problem is especially acute in the analysis in such particles as H, O and OH, for which there is a high probability of heterogeneous recombination on metals [6].

The application of a modulated beam to the mass spectrometric analysis of free radicals has been described by Foner and Hudson [7]. In distinction to their construction, the molecular and the ion beams are not perpendicular in our apparatus but coaxial. This permits an improvement in the ratio of the ion signal for the molecular beam to the ion current due to molecules of the residual gases in the apparatus and to scattered particles from the analyzed mixture. Such an improvement is in order in view of the fact that at the slit width which was used, the ions resulting from the particles of the molecular beam have a much greater likelihood of coming from the source.

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* The development of the apparatus was carried out by V. L. Talroze, L. L. Dekabrun, G. D. Tantsyrev and A. K. Lyubimova (the electronic subassemblies of the apparatus have in part been described in [8, 14]).

The system for forming the molecular beam and the scheme for attaching the discharge unit to the mass spectrometer are shown in Fig. 1. The molecular beam was formed by the injection diaphragm 5 and by narrow canal 6 (the canal consisted of two parts: a narrower with d = 0.15 mm, l = 3 mm and a widener, d = 0.6 mm, l = 13 mm). Between these there was inserted the shutter 7 for modulating the beam, this being affixed to a bellows and moved either manually or with the aid of an electro-magnetic relay. The pressure in the region 8 amounted to 10^{-3}-10^{-4} mm of Hg. (The distance between the injection diaphragm and the canal was 7 mm; that between the canal exit and the ion source, 30 mm).

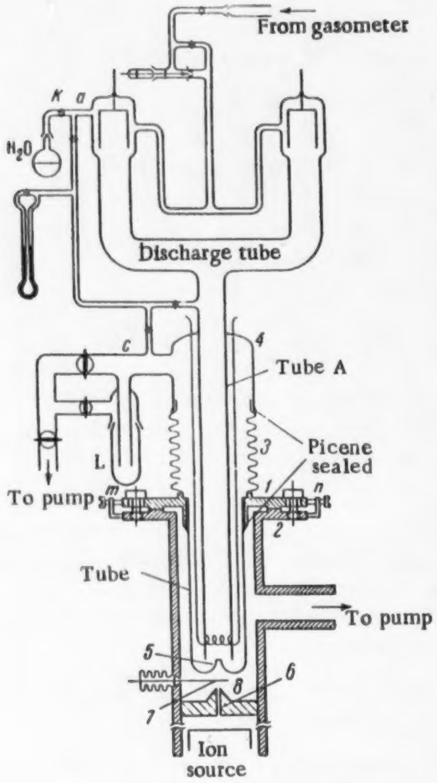

Fig. 1. Diagram of the apparatus.

The injection diaphragm was in the form of a Pyrex cap with a flat bottom, ~30μ in thickness, and an orifice for which d ~ 150μ. The technique of preparing such diaphragms has been described in [9]. The pyrex tube B with the diaphragm was vacuum-sealed to the flange 1 which in turn was joined to the exhaust tube 4 through the bellows 3. With the aid of the screws n, m it was possible to displace flange 1 with respect to flange 2 along a ground surface, this permitting alignment of the system. The distance between the discharge tube and the diaphragm amounted to 300 mm. The water vapors passed into the discharge tube from a bulb with a cock K and were drawn through the tube A and a trap L which was cooled with liquid nitrogen and served as a powerful pump when the degree of decomposition of the water in the discharge was low. The pressure was measured at the points a, b and c by a U-tube oil manometer and was regulated by the cock K and by the temperature of the bath containing the bulb with the water. The walls of the discharge tube and tube A were treated with concentrated metaphosphoric acid.

1. Calibration of the mass spectrometer with respect to H and O atoms. Calibration of the apparatus was carried out with respect to the atoms of H and O, these being obtained by drawing hydrogen and oxygen respectively through the discharge. The number of atoms in the stream was determined from the amount of heat which was evolved by their recombination on a platinum spiral placed between the tubes A and B at a distance of 5 mm from the diaphragm (the diameter of the wire was 0.1 mm; the spiral was attached to thin glass fibers sealed to the outer surface of the tube A). The spiral was a part of a bridge measuring circuit. The evolution of heat on the wire resulting from the recombination of atoms during discharge was compensated for by adjusting the heating of the wire so that its temperature (i.e., its resistance) remained constant.

In such measurements it is necessary that all of the atoms recombine. In order to determine the extent to which this condition was fulfilled, a second Pt spiral was inserted behind the first and close to it. On the second spiral the amount of heat liberated was 10-15 times less than on the first. This permitted the conclusion that ~ 90% of all the atoms recombined on the first spiral.

In the calibration experiments the concentration was found to be equal to 30% both for the H and for the O atoms. Along with the determination of the concentrations of the atoms in the jet, there were measured the modulated components of the ion currents with (I') and without (I") discharge. The values of I', I" and I' - I" are shown in Table 1. The pressure in this experiment was 0.8_2 mm of Hg. In the case of the H, the ion current which arises strictly from the atoms, was equal to $I_H = (I' - I'')_{m/e=1} K_{H_2} (I' - I'')_{m/e=2}$, K_{H_2} being the ratio of the intensities of the lines at 1 and 2 amu in the mass spectrum of H_2 as determined without the discharge. The value of the ion current for the O atoms was determined in a similar fashion.

TABLE 1

Hydrogen, electron energy 66 v				Oxygen, electron energy 30 v			
m/e	I'	I''	$I'-I''$	m/e	I'	I''	$I'-I''$
	mm scale				mm scale		
1	41	21	20	16	280	190	90
2	460	534	−74	32	210	360	150

TABLE 2

m/e	I'	I''	$I'-I''$	I	Electron energy, v
	In scale units				
1	80	65	15	5	66
2	60	0	60		66
16	51	16	35	23	30
17	288	250	38	10	30

The sensitivity of the apparatus, η, defined as the ratio of the partial pressure of the atoms to the value of the corresponding ion current, I, was equal to

$$\eta_H = 1.25 \cdot 10^{-2} \frac{\text{mm of Hg}}{\text{mm scale}}, \quad \eta_O = 2.7 \cdot 10^{-3} \frac{\text{mm of Hg}}{\text{mm scale}}.$$

For the validity of such a calibration it is essential that the ion current be proportional to the pressure in the tube A over the entire range of working pressures.

In Fig. 2 there is shown a calibration for the apparatus in terms of the pressure of O_2 using the line m/e = 16. As is to be seen from Fig. 2, a direct proportionality is observed up to a pressure of 6 mm of Hg.

2. The results of mass spectrometric measurements of the concentrations of atoms and radicals in the discharge products from water vapors. Measurements were carried out at pressures of 0.5-4 mm of Hg and with a discharge current of 100-150 ma. The intensities of the ion currents I', I" were measured for m/e = 1; 2; 16; 17; 18 and 32.

With water vapor pressures of 0.5-1.5 mm of Hg in the discharge, atomic H and free hydroxyls were observed, but no O atoms could be found. An evaluation in terms of the sensitivity of the apparatus indicated that the concentration of the O atoms was in every case less than that of the OH. O atoms were observed on raising the pressure to 3 mm of Hg. The results of measuring the concentrations of the atoms of H and O and the free hydroxyls are presented in Table 2 (the velocity of the jet amounted to 30 m/sec, the degree of transformation of the water to 3-4%).

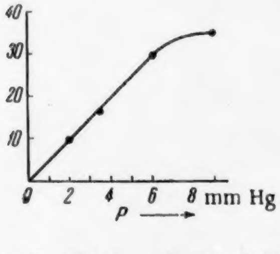

Fig. 2. The dependence of the intensity of the m/e = 16 line in the mass spectrum of O_2 on the pressure in front of the injection diaphragm.

The values of the ion current I in Table 2 were completely determined by the H and O atoms and the free hydroxyls. They were obtained by subtracting from the I' −I" values for the lines m/e = 1, 16 and 17 the corresponding values due to the dissociative ionization of H_2, H_2O and O_2 (the value of K_{H_2O} was found in a separate experiment).

The concentrations of the H and the O atoms and the free hydroxyls were obtained by multiplying the values of I by the respective sensitivity coefficients and proved to be equal to: [H] = 0.06 mm of Hg, [O] = 0.06 mm of Hg and [OH] = 0.03 mm of Hg. These values were accurate to within a factor of 1.5-2. The concentration of O_2 amounted to 0.04 mm of Hg, i. e., it was less than the concentration of the O* atoms. In calculating the value of [OH] we assumed that $\eta_0 = \eta_{OH}$. Such an assumption is justified to within at least 20-30%, since the number of electrons in these particles differs by only 12 and the intensity of the 16 line in the mass spectrum of the free hydroxyls does not exceed 25% of the intensity of the 17 line, even at 70 ev [10]. (The fact that the intensity of the 16 line in the mass spectrum of OH is less than that of the 17 line is also indicated by our experiments at low pressures, the OH being disclosed from the excessive intensity of the 17 line though it could not be found from the excess intensity of the 16 line).

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* O_3 and H_2O_2 were not detected in the mass spectra.

Thus mass spectrometric measurements confirm the presence of O atoms at appreciable concentration in the discharge products from water vapors. The question remains as to the mechanism of their formation in the discharge.

From the recently established fact of the absence of an energy of activation in ion-molecular reactions [11-12] it follows that at least two processes must lead to the formation of O atoms in the discharge.

$$OH^+ + H_2O \rightarrow O + H_3O^+ + 58 \text{ kcal/mole}$$
$$OH + H_2O^+ \rightarrow O + H_3O^+ + 47 \text{ kcal/mole}$$

On elevating the pressure, these processes must play a greater and greater role. It is possible that it was exactly this fact which was responsible for the earlier view as to the small fraction of O atoms in the discharge products in water vapors, since this opinion rested on work which had been carried out at low pressures (tenths of a millimeter of Hg) and was in contradiction with the experiments of Avramenko which were performed at a pressure of several millimeters of Hg. This hypothesis also agrees with the fact that O atoms were not detected by us in the region of lower pressures.

The authors are indebted to Academician V. N. Kondratyev for valuable discussions and to A. A. Bulatova for assistance in the work.

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THE FORMATION OF DI- AND TRIVALENT SILVER ON A ROTATING DISK ELECTRODE IN ALKALINE SOLUTIONS

Yu. V. Pleskov

(Presented by Academician A. N. Frumkin. May 21, 1957)

There have been a number of papers devoted to the electro-oxidation of silver. The anodic discharge curves for silver electrodes in NaOH solutions have two plateaus, the potentials of which are close to the reversible potentials $\varphi_{Ag/Ag_2O} = 0.344$ v and $\varphi_{Ag_2O/Ag_2O_2} = 0.57$ v. There is a third plateau corresponding to the evolution of oxygen. It is clear that Ag is reversibly oxidized to Ag_2O, and even to Ag_2O_2, at sufficiently low current densities [1]. According to another view, Ag_2O_2 does not result from the electrode process directly but arises from the breakdown of a higher silver oxide which is initially formed on the electrode [2].

During oxidation by ozone in NaOH solutions, powders of Ag and Ag_2O acquire a potential approximating the reversible potential $\varphi_{Ag_2O_2/Ag_2O_3} = 0.79$ v. On removing the oxidizing agent, the potential falls to that of φ_{Ag_2O/Ag_2O_2}. It is obvious that for practical purposes trivalent silver is unstable in alkaline solutions [3]. Mixed compounds of mono-, di- and trivalent silver are formed during the oxidation of Ag^+ ions in neutral and acid solutions containing the anions NO_3^-, ClO_4^-, SO_4^{-2} and F^- [4].

The ions of di- and trivalent silver are thermodynamically unstable in aqueous solution [5].

The solubility of Ag_2O in concentrated KOH solutions has been determined jointly by B. N. Kabanov and ourselves [6] and it was shown that the ions of monovalent silver form a univalent complex containing three silvers, the composition being expressed by the formula $[Ag_3O(OH)_2]^-$.

Up to the present there has been no elucidation of the mechanism of the oxidation of a silver electrode in an alkaline electrolyte. In particular, it is not known whether the oxidation proceeds in the solid phase or whether the silver ions enter into solution and then undergo discharge at the electrode. Thus it has seemed to us to be of interest to study the anodic oxidation and reduction of alkaline Ag_2O solutions.

We have employed a gold electrode as an anode, this being activated prior to each measurement by alternate cathodic and anodic polarization in 1 N H_2SO_4. We have obtained curves in Ag_2O saturated KOH solutions (8.4-13.4 gew/l) at various speeds of rotation of the electrode; by way of example, one of these curves is shown in Figure 1 (Curve 1).

Simultaneously with the oxidation of Ag_2O, the parallel process of oxygen evolution occurs at the anode. We have applied the method of the rotating disk electrode in order to distinguish the current which arises from the silver oxidation and depends on the intensity of agitation, from the current due to the discharge of hydroxyl ions, which, at the given concentrations of alkali and current strengths, is independent of the agitation. A quantitative theory of convectional diffusion to the rotating disk has been developed by V. G. Levich [7] and subsequently confirmed experimentally [8]. In the case of an electrochemical process whose rate is determined by diffusion of the reacting particles to the electrode, there is, according to the Levich theory, a direct proportionality between the current strength and the square root of the angular velocity of rotation of the electrode, ω, when a fixed concentration difference exists between the body of the solution and the disk surface; extrapolation of $\omega = 0$ at a constant value of the concentration polarization must give the result $i = 0$. In our case it turns out that the value of the current i at fixed potential depends linearly on $\sqrt{\omega}$ (Fig. 2). Extrapolating the straight lines which have been experimentally obtained at various potentials to $\omega = 0$ (Fig. 2), we have separated out that part of the total current which is independent of the rate of rotation of the electrode (Fig. 1, 2). The calculated Curve 2 corresponds to the evolution of oxygen.

By subtracting the current density corresponding to Curve 2 from the total anodic current (Fig. 1, 1) we have obtained a calculated polarization curve for the oxidation of Ag_2O (Fig. 1, 3). This curve shows two waves, of amplitude proportional to the value of $\sqrt{\omega}$ and the concentration of the monovalent silver in solution, and is thus fixed by the rate of diffusion of the $[Ag_3O(OH)_2]^-$ ions to the electrode. The first wave corresponds to the oxidation of these ions to Ag_2O_2 which as a black deposit gradually covers the electrode

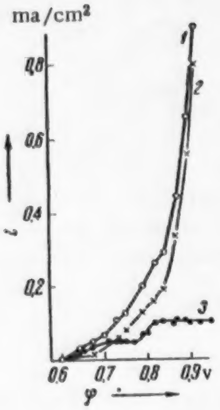

Fig. 1. Anodic polarization curves obtained with a rotating gold disk electrode in a $2.3 \cdot 10^{-4}$ N solution of Ag_2O in 13.4 N KOH. Rotation rate of the electrode, 3100 rev./min. 1) Experimental curve; 2) calculated curve for the evolution of O_2; 3) calculated curve for the oxidation of Ag_2O.

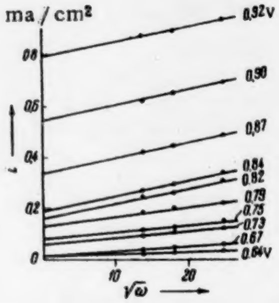

Fig. 2. The relation between the current density (Fig. 1, 1) and the angular velocity of rotation of the electrode.

$$2[Ag_3O(OH)_2]^- + 4OH^- \rightleftarrows 3Ag_2O_2 + 4H_2O + 6\bar{e}.$$

The density of the limiting current (wave amplitude) is equal to the value of the limiting current from the experimentally determined cathodic polarization curve for the reduction of silver ions to metallic silver in these same solutions (Fig. 3). The second wave is twice as high as the first and, thus, corresponds to the oxidation of $[Ag_3O(OH)_2]^-$ to the oxide of trivalent silver. In each case oxidation is accompanied by a pronounced overvoltage, the slopes of both waves in the semilogarithmic system of coordinates (0.09 and 0.06 respectively) being greater than the values calculated from the equation for concentration polarization (0.058 and 0.029).

Thus, using this new method for distinguishing the diffusional and non-diffusional currents on the rotating disk electrode, it has been definitely proven that by anodic polarization in strong alkali the silver of Ag_2O is oxidized to Ag_2O_2 and to trivalent silver, at sufficiently high potentials. The value of the current is determined by the rate of diffusion of the monovalent silver ion to the electrode; consequently the processes of oxidation and reduction of the silver oxide can pass through the solution at high velocity.

In carrying out these experiments we have found that the potential of an electrode covered with the oxides of di- and trivalent silver at $\varphi = 1.0$ v immediately falls on discontinuing the anodic polarization and after several minutes takes on a value of 0.6 v; no observable leveling off was noted at the potential of the system Ag_2O_2/Ag_2O_3. It is clear that trivalent silver is very unstable in alkaline solutions.

We have made an attempt to evaluate the stability of the Ag^{II} ions. In a KOH solution above a precipitate of Ag_2O_2 (which was obtained by the oxidation of $AgNO_3$ with $K_2S_2O_8$, [9]), the potential of a rotating nonpolarized platinum electrode takes on the value 0.34 v, the stationary potential of Ag in alkaline solutions of Ag_2O. The cathodic polarization curve obtained in this solution has such a limiting current as would indicate the solution to be saturated with Ag_2O. This solution was subjected to anodic oxidation at the gold electrode under a potential of 0.73 v (with reference to the cathode) for several days in order to remove traces of possible reducing agents. During this time the potential of a rotating nonpolarized platinum electrode immersed in the solution gradually changed from 0.34 to 0.57-0.62 v. Thus a satisfactorily high concentration of the divalent silver was produced in solution and this together with the monovalent silver, fixed the potential. Interrupting the rotation of the platinum electrode resulted in a sharp decrease of its potential which, on the resumption of rotation, again rose, taking on a value of about 0.6 v. With cessation of anodic polarization of the gold electrode, the potential of the rotating platinum electrode gradually fell over several hours to 0.34 v. It is clear that the cause of this effect is to be found in the fact that the ions of divalent silver are unstable in aqueous solution and undergo gradual reduction to monovalent silver with the evolution of oxygen or the oxidation of dust particles which have accidentally entered the system. It is possible that the platinum slowly and extensively oxidizes, reducing the silver ion to Ag and then to the metal.

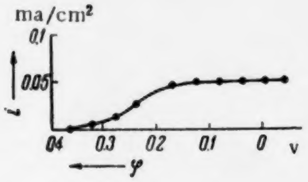

Fig. 3. A cathodic polarization curve obtained on a rotating disk electrode in $2.3 \cdot 10^{-4}$ N solution of Ag_2O in 13.4 N KOH. Rate of rotation of the electrode, 3100 rev./min.

The instability of the Ag^{II} ions is also indicated by the fact that on dissolving a chemical precipitate of Ag_2O_2 or an anodic precipitate of the latter obtained on the gold electrode, in a concentrated solution of KOH, the silver enters solution only in the form of the Ag^{I} ions (as was proven from the cathodic polarization curve in the solution).

Despite the low stability of the Ag^{II} ions in solution, the data which have been obtained make it possible to conclude that the oxidation-reduction processes on a silver electrode in an alkaline electrolyte can proceed not only in the solid phase but also through the solution.

I wish to express my deep appreciation to Academician A. N. Frumkin for proposing this problem and to Professor B. N. Kadanov for valuable advice in the course of a discussion of the results.

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THE PROPERTIES OF INTERMEDIATE CARBON-OXYGEN COMPOUNDS

S. I. Rempel

(Presented by Academician A. N. Frumkin. May 21, 1957)

It can be considered as an established fact that intermediate carbon-oxygen compounds are formed during the activated sorption of oxygen by charcoal.

We, in particular, have advanced the hypothesis of the formation of intermediate oxides of carbon [1, 2] in establishing a mechanism for the processes which are responsible for the high overvoltages at carbon anodes in aluminum baths. According to this mechanism, the production of electrochemically active, intermediate carbon-oxygen compounds is the initial result of the discharge of oxygen-containing ions at a carbon anode. In time, the bonds between the chemosorbed oxygen and the carbon lattice are redistributed and strengthened, the final result being the formation and desorption of gaseous oxides of carbon. Due to the energetic nonuniformity of a carbon surface, discharge at low current density takes place on its most active regions, the strongest bonds being formed between the oxygen and the carbon at relatively low anodic potentials (which very nearly correspond to the free energy of the reaction $Al_2O_3 + 3C = 2Al + 3CO$). With an increase in the current density, the discharge is extended to the less active regions as well; here discharge is possible only at a higher potential because of the diminished energy of oxygen sorption. Consequently there is at higher potentials an ionic exchange of oxygen between the intermediate oxides formed on the anode at the higher potentials and the oxygen-containing ions in the electrolyte; this is observed over many minutes, even after the reduction of the current density by 30%. It is clear that pure CO_2 is evolved at the industrial current densities as the result of electrochemical desorption.

It is this step of the formation and desorption of the gaseous oxides of carbon which is the slow one and it leads to the existence of an anodic overvoltage in the aluminum baths.

The present communication contains another proof of the fact that the potential of the carbon anode at 960° is not determined by the partial pressure of O_2 in the gas bubbles below it, as was believed earlier, nor by the overvoltage of the O_2 evolution, but solely by the electrochemically active carbon-oxygen compounds which have been formed at high anodic potential, the overvoltage arising from their delayed decomposition.

The arrangement of the experiments which are described below is based on a procedure which has been used with aqueous solutions since 1937 [3].

The carbon anode $\underline{2}$ (Fig. 1), which had the form of a small tube closed at one end, was polarized from the outer side. Within it there was a small amount of the electrolyte and a carbon rod $\underline{1}$, which served as an oxygen-carbon comparison electrode [4]. Measurements of the potential of the carbon anode (on its diffusional side) against the oxygen-carbon reference electrode were carried out with a lamp potentiometer having an input resistance of $2 \cdot 10^7$ ohm.* During these experiments the current between the anode and the iron diaphragm cathode was maintained at essentially constant strength. In the first series of experiments a $KCl-NaCl-Na_2SO_4$ mixture (mp 565°) served as the electrolyte. The thickness of the bottom of the carbon tube amounted to 1.0-1.5 mm; its external diameter to 13 mm.

Some time after closing the circuit the potential of the anode on the inner, diffusional side began to increase. Thus in one of the experiments the results of which are shown in Fig. 2, even 20 seconds after beginning electrolysis with a current of 1.0 amp., the potential on the diffusional side of the anode stood 0.24 v more positive than the carbon reference electrode.

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[*] In view of the small volume of the electrolyte it is likely that there was a large change in its composition due to the formation of electric double layers and selective adsorption of the components of the melt, but this is without significance since the anode and the comparison electrode were constructed from the same material.

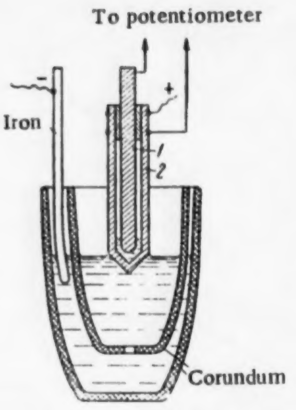

Fig. 1. The measuring cell with the carbon tube anode, the carbon-oxygen comparison electrode being inside the latter.

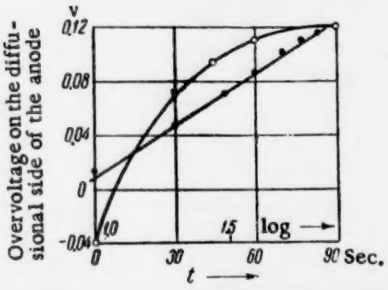

Fig. 2. The dependence of the overvoltage at the inner, polarized surface of the carbon anode on the time elapsed after beginning the electrolysis. Electrolyte, KCl–NaCl–Na_2SO_4 at 650°.

There was no abrupt change in the anodic potential on breaking the circuit (which indicated the absence of an IR component); its value began to gradually diminish and after 2 minutes became equal to the potential of the comparison electrode. The same picture was observed after a second passage of the current. The curve in Fig. 2 was constructed from recordings of the anodic potential on the diffusional side during one passage of the current (at a strength of 0.3 amp. and a temperature of 650°).

In another series of experiments an alumina-cryolite melt (Na_3AlF_6, 60.5 weight %; Al_2O_3, 4 weight%; AlF_3, 35.5 weight %) served as the electrolyte. After 30 minutes of electrolysis at a current strength of 1.3 amp., the potential on the diffusional side had risen to 0.125 v and continued to increase (Fig. 3). In this case the thickness of the bottom of the carbon tube anode, prior to the experiment, amounted to 3 mm and the potential on the diffusional side increased very slowly; at the end of the experiment the bottom thickness was only 0.5-0.7 mm. Here, in distinction to the experiments of the first series, the potential on the diffusional side fell to zero almost as soon as the circuit was broken. It is possible that this is completely, or in part, to be explained by the higher temperature (higher by 100°). It is interesting to note that if the current was lowered by only 30% the potential on the diffusional side remained unchanged during at least 2 minutes (in the course of an observation). This observation agrees with our measurements on the polarized side [1, 2].

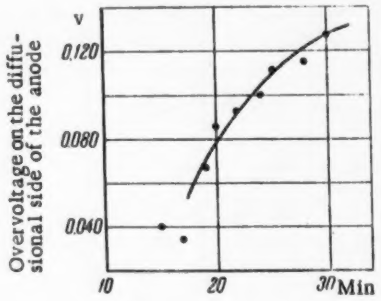

Fig. 3. The dependence of the overvoltage on the inner nonpolarized surface of the carbon anode on the time elapsed after beginning electrolysis. Electrolyte; alumina-cryolite melt at 950°.

The gradual appearance of an overvoltage on the nonpolarized, inner side of the carbon tube anode confirms the above outlined mechanism of the establishment of this potential; it is completely impossible of explanation from the point of view of earlier theories.

In addition to this basic conclusion, it is in order to point out the following. In the last experiment (at 770°) the linear rate of erosion of the carbon anode amounted to about 5 mm per hour. Thus the rate of penetration of the chemosorbed oxygen to the diffusional side could not have been less than this figure. Judging from Fig. 2, the rate of penetration of oxygen through the carbon at 670°, i. e., at a still lower temperature, may have been considerably greater and possibly even exceeded 1 mm per minute.

Qualitatively this same correspondence of rates has been observed in other experiments as well. There is nothing paradoxical in this, since the potential difference between the diffusional side of the anode and the oxygen-carbon comparison electrode arises only because of oxygen-carbon compounds of nonequilibrium composition which are formed at a potential considerably in excess of the reversible potential. At the higher temperatures, the rate of redistribution of the bonds between the oxygen and the carbon lattice is greater and the combustion reaction proceeds in a more shallow layer of carbon on the polarized side.

Finally it is noteworthy that the relation between the time and the overvoltage on the diffusional side was strictly logarithmic (Fig. 2).

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THE CRITICAL CONDITIONS FOR THE IGNITION OF COMBUSTIBLE GASEOUS MIXTURES BY HEATED SOLID BODIES

A. I. Rozlovsky

(Presented by Academician V. N. Kondratyev. June 28, 1957)

The question of the possibility of igniting combustible gaseous mixtures by heated bodies is one of much practical interest both in the problems of motor operation and in accident prevention. Ya. Z. Zeldovich [1] has obtained an approximation for the critical condition for the existence of a stationary thermal regime during ignition by an infinite plane wall at the constant temperature T_s,

$$q_{\mathrm{cr}}^2 = 2\lambda h \int_{T_0}^{T_s} \Phi(a_1, T)\, dT. \tag{1}$$

q_{cr} being the critical value of the thermal flow from the reaction zone, per unit of ignition surface; λ, the thermal conductivity; h, the heat of reaction; Φ, the reaction rate; a, a dimensionless constant expressed in grams/1 gram of mixture and the index 1 designating the deficient component whose concentration fixes that part of the mixture which is capable of reacting, variation in the concentrations of the remaining components being neglected in the first approximation.

Neglecting the dependence of Φ on the concentration of the mixture which is being depleted near the surface, Ya. B. Zeldovich obtained

$$q_{\mathrm{cr}}^2 = 2\lambda\theta h \Phi(T_s), \tag{2}$$

where $\theta = RT_s^2/A$ is a characteristic temperature interval and A is the energy of activation. In [2] this solution has been made more precise by taking into account the variation in concentration and the similitude of the fields of T and a [3]. With a constant heat capacity, c

$$a_1/a_{01} = (T_b - T)/(T_b - T_0), \tag{3}$$

the indices 0 and b refering to the initial state of the mixture and to the products of its combustion. •

• We will prove the validity of a condition of similitude for the problem in question. When thermal diffusion is neglected, the equations for thermal conduction and diffusion in the X direction take the forms:

$$\frac{d}{dx}\lambda\frac{dT}{dx} + h\Phi(a_1, T) = 0, \quad \frac{d}{dx}D\rho\frac{da_1}{dx} - \Phi(a_1, T) = 0,$$

where D is the coefficient of diffusion and ρ is the density. Introducing the variable $H = \int_0^T c\,dT$, we find $\frac{dH}{dx} + \frac{Dc\rho}{\lambda}\frac{d(a_1h)}{dx} = \mathrm{const.}$. For a mixture of gases of approximately equal molecular weights, in which there is equality of the coefficients of diffusion and thermal conductivity ($\lambda/c\rho$), $d(H + a_1h)/dx = \mathrm{const.}$ Since at the surface, $dT/dx = 0$ and $da_1/dx = 0$, const = 0, in the absence of a catalyst, $H + a_1h = \mathrm{const}' = H_0 + a_{01}h$, from this (3) follows.

We would like to mention a special detail which has not been noted earlier. The solution of Ya. B. Zeldovich describes only that case in which the temperature of combustion, T_b, exceeds the ignition temperature, T_s. It follows from (3) that the reaction is fully completed at the surface when $T_b = T_s$, i. e., the propagation of a normal flame then becomes possible. This indicates that a combustible mixture must be ignited by any heated, catalyticly inactive, body for which $T_s \geq T_b$. Experiment shows that such is not always the way of it, ignition being subjected in this case to other laws. It has been shown in [1] that Equation (1) is applicable to the nonplanar case provided that the radius of curvature of the igniting surface is large in comparison with the parameter $\sqrt{\lambda\theta/h\Phi\ (T_s)}$, this latter being equal in order of magnitude to the width of the reaction zone in the flame, a quantity which does not exceed several tenths of a millimeter even in slow flames.

In calculating the thermal expansion it is assumed, just as in [2], that $T_0/T \approx T_0/T_s$, Φ being small outside the limits of a comparatively narrow temperature interval close to T_s. This gives $\Phi = Ba_1^{s_1}(T_0/T_s)^s e^{-A/RT}$, where B is the multiple of the exponential in the expression for the velocity constant, s is the total reaction order and s_1 is the reaction order for the deficient component. Expanding the exponent in a series [4], we obtain

$$q_{cr}^2 = 2\lambda hBe^{-A/RT_s}(T_0/T_s)^s [a_{01} / (T_b - T_0)]^{s_1} \int_{T_0}^{T_s} (T_b - T)^{s_1} e^{-(T_s-T)/\theta} dT \,. \tag{4}$$

The authors of [2] have assumed that $s = s_1 = 2$, although it is not $s = s_1 + s_2$ (s_2 refers to the component present in excess) which enters into the expression under the sign of integration in (4) but s_1, which can scarcely be greater than unity. Supposing $s_1 = 1$, we find

$$\begin{aligned} q_{cr}^2 &= 2\lambda hBe^{-A/RT_s}\theta (T_0/T_s)^s [a_{01}/(T_b - T_0)] [T_b - T_s + \theta - e^{-(T_s-T_0)/\theta} \times \\ &\times (T_b - T_0 + \theta)] \approx 2\lambda hBe^{-A/RT_s} a_{01} (T_0/T_s)^s \theta (T_b - T_s + \theta)/(T_b - T_0) = \\ &= 2\lambda\theta h\Phi (a_{01}, T_s) (T_b - T_s + \theta)/(T_b - T_0). \end{aligned} \tag{5}$$

Thus with $s_1 = 1$ the exact solution differs from the approximation expression of (2) by the coefficient $(T_b - T_s + \theta)/(T_b - T_0)$; in the solution of [2] this correction must amount to $(T_b - T_s)(T_b - T_s + 2\theta)/(T_b - T_0)^2$; it being noted that it is not always true that $T_b - T_s \gg 2\theta$.

For the ignition of a mixture of gases markedly differing from one another in molecular weight, $\vartheta = Dc\rho/\lambda \neq 1$. Supposing ϑ to be constant, we find:

$$d(H + \vartheta a_1 h)/dx = \text{const} = 0;\ H + \vartheta a_1 h = \text{const}' = H_b. \tag{6}$$

It follows from this that the condition $(T_b - T)/(T_b - T_0) = \vartheta a_1/a_{01}$, is fulfilled in the ignition of a mixture with $\vartheta \neq 1$ and is also approximately valid for the reaction zone in the combustion of such mixtures [5]. In this case the expression for q_{cr}^2 is altered only through the constant factor $1/\vartheta^{s_1}$.

We will express the quantity q_{cr} in terms of the dimensionless criteria of similitude as $q_{cr}(T_s) = \lambda(T_s - T_0)\,\mathrm{Nu}/d$, d being the characteristic dimension of the igniting body. In the high temperature region, $\lambda \sim \sqrt{T_s}$ for the external problem with $\mathrm{Re} > 200$ $\mathrm{Nu} = 0.54\sqrt{\mathrm{Re}}$ [6]. From this it follows that

$$e^{A/RT_s} \sim \frac{(T_b - T_s + RT_s^2/A)\,T_s^{0.5-s_1}}{(T_s - T_0)^2}\,\frac{d}{v} = \varphi_1 \quad \text{when } s_1 = 1; \tag{7}$$

$$e^{A/RT_s} \sim \frac{(T_b - T_s + 2RT_s^2/A)(T_b - T_s)}{(T_s - T_0)^2\,T_s^{s_1-0.5}}\,\frac{d}{v} = \varphi_2 \text{ when } s_1 = 2, \tag{8}$$

where v is the velocity of the gas stream.

In fixing the reaction order we will make use of the data on the influence of the pressure, p, on the normal flame velocity, u_n. For a number of air-hydrocarbon mixtures $u_n \sim p^{-g}$ [7-9], g ranging in value from 0.25 to 0.40. It is known that $s = 2(1-g)$ if the products of combustion are not dissociated [10]. For the mixtures under consideration it can thus be supposed that the total order of reaction is somewhat greater than the first. Since it is posssible that $s_1 > s_2$, our supposition that $s_1 \approx 1$ cannot be considered as unreasonable.

We will consider the extent to which this theory agrees with the experimental data of [11, 12], comparing the results of calculations with the estimated values of [2]. It is first necessary to obtain at least approximate evaluations of the energy of activation since this determines θ. In [13] values of A have been calculated for a number of air-fuel mixtures; for pentane $A = 26$ kcal/mole and for hydrogen, 16 kcal/mole.

From the data of [11] on the function $T_s(d)$ for a 3% pentane mixture ($T_b = 2222°$ K, $v = 4$ m/sec), we find on setting $s_1 = 1$, $s_2 = 0.5$ that the points in a plot of $\log \varphi$ vs $1/T_s$ fall satisfactorily on a straight line with a slope corresponding to $A = 27$ kcal/mole, this being in good agreement with independent data [13]. For pentane with $s_1 = 2$ and the above indicated simplifications, there was obtained in [2], $A = 35\text{-}36$; supposing $s_1 = 2$, $s_2 = 0$, we find from (8), $A = 33$. For a mixture with 20% H_2 ($T_b = 1853°$ K)[11], a like calculation with $s_1 = 1$, $s_2 = 0.5$ gives $A = 38.5$ in the low temperature region and $A = 20$ in the high temperature region; in other variants of this calculation the values obtained are larger by 4-7 kcal/mole. If the composition of the illuminating gas referred to in [11] was the same as that of [12], $T_b > T_s$ only for the richest of the mixtures studied in [12]. Analysis of the $T_s(d)$ relation for a mixture including 20% of illuminating gas (H_2, 50%) with $v = 1.2$ m/sec, $T_b = 2330°$ K, $s_1 = 1$ and $s_2 = 0.5$, gives $A = 32.5$.

Analysis of the $T_s(v)$ relation for mixtures of illuminating gas with 16 and 20% fuel gas [12], using $s_1 = 1$, gives an effective $A = 23$ kcal/mole at the higher v's (higher T_s's), this value increasing 2-4 fold for the smaller of the investigated T_s. Under these conditions the critical T_s depends strongly on the material of which the igniting body is composed, this effect increasing with a rise in the flow velocity. This is to be seen still more clearly in the experiments of [14] in which a turbulent stream was ignited by heated rods. Thus the effective A for pentane increased several fold, starting from a value of the order of 11-12 kcal/mole. Here the effect of the rod material was particularly great: by replacing stainless steel with platinum at $d = 6.3$ mm and $v = 72$ m/sec, the critical temperature, T_s, of a stoichiometric pentane-air mixture was increased by 430°.

All of these details which have gone unnoticed up to the present time are probably tied up with clear cut catalytic surface activity which has resulted in the transfer of the reactions out of the kinetic into the diffusional region [6]. At low rates of flow, ignition occurs at low T_s; it is purely homogeneous and its critical conditions do not depend on the properties of the surface which here plays the role of a mere source of heat. Even in [11] it is possible to see the beginning of a transition into the diffusional region in certain changes of T_s during the ignition of hydrogen by quartz and platinum spheres. The transfer to diffusional (catalytic) combustion finds its expression in a diminution of the effective energy of activation, the depletion of the mixture near the surface by heterogeneous reaction bringing about an increase in the critical T_s. We note that reaction proceeds at low flow rates in the kinetic region and not inversely, as is the case under isothermal conditions.

We will now explain why an increase in the temperature affects the catalytic reaction more strongly although its energy of activation, A_c, is usually less than the corresponding quantity, A_h, for the homogeneous process. The amount of material which reacts on homogeneous ignition is $m_h = q_{cr}/h \sim \sqrt{\Phi(T_s)} \sim e^{-A_h/2R}{}_s$. The corresponding quantity for the catalytic reaction is $m_c \sim e^{-A_c/RT_s}$. Thus a temperature increase will act more strongly on the heterogeneous reaction if $A_c > A_h/2$ (compare with [15]). On the other hand, the increase in v which accompanies a rise in temperature accelerates the transfer of matter to this surface and this also indicates a heterogeneous reaction.

It is also possible to calculate absolute values for the critical conditions of combustion, starting from the known properties of the combustible mixtures. For this purpose it is useful to replace the difficultly determinable quantity, the reaction rate Φ, by a macroscopic characteristic of the combustible mixture, its normal flame velocity. For all the cases which are of practical importance, the theory of normal combustion [3, 5] gives;

$$u\rho \Big/ \sqrt{\frac{1}{a_{01}} \Phi(a_{01}, T_b) \frac{\lambda}{c}} = \sqrt{\frac{2s_1!}{\vartheta^{s_1}} \left(\frac{\theta}{T_b - T_0} \right)^{s_1+1}} \quad . \tag{9}$$

We will compare the parameters for the normal combustion of a mixture of the indicated components which has a combustion temperature T_s, a corresponding initial concentration a_s, density ρ_s and normal flame velocity u_s, with the critical conditions for the ignition by a heated body of a mixture of concentration a_{cr}. With $s_1 = 1$, Equations (9) and (4) give:

$$u_s = \frac{\dot{\lambda}}{c\rho_s}\frac{\mathrm{Nu}}{d}\sqrt{\frac{\pi_s}{\pi_{\mathrm{cr}}}\,\frac{T_b - T_0}{T_s - T_0}\,\frac{\theta}{T_b - T_s + \theta}} = ,$$

$$= 0.54\,\frac{\lambda}{Q}\sqrt{\frac{\overline{M}RT_0v\,(T_b - T_s)\,(T_s - T_0)}{p\eta d\pi_s\pi_{\mathrm{cr}}\left(\frac{T_b - T_s}{\theta} + 1\right)}}. \qquad (10)$$

Here π is the mole fraction of the deficient component, Q is the molar heat of combustion, $\overline{M}$ is the mean molecular weight of the combustible mixture and η is the viscosity. Equation (10) is valid regardless of the value of ϑ, since the added factor $1/\vartheta^{s_1}$ enters into the expressions for both q_{cr} and u_s.

For the above-mentioned pentane-air mixture [11] with d = 3.6 mm, $T_s = 1373°$ K; $\pi_s = 1.122\%$, $v = 4 \cdot 10^2$ cm/sec. Supposing that A = 25 kcal/mole, we find $u_s = 2.7$ cm/sec. According to the data of [16] on lean mixtures of air with a number of hydrocarbons (CH_4, C_2H_6, C_2H_4, C_3H_8, C_4H_{10}), $u_n = 0.794/\left(1 - 2.206 \times \pi\frac{Qp}{RT_0}\right)$, from which we find for a mixture of 1.122% pentane, $u_s = 4.2$ cm/sec, a result which is in satisfactory agreement with the calculated value.

For methane with d = 6.5 mm, $\pi_{cr} = 8.0\%$ $T_b = 2052°$ K; $T_s \approx 1473°$ K, $\pi_s = 5.0\%$. Supposing that A = 26 kcal/mole [13], we find $u_s = 2.9$ cm/sec. According to [16] and [17], a 5% methane-air mixture is near the concentration limit for flame propagation and for this the value $u_n \approx 3$ cm/sec has been fixed in [17]. From what has been said it follows that the critical conditions for ignition by a heated surface can be calculated with considerable accuracy from data on flame velocities in lean mixtures near the propagation limit. When a catalytic effect exists, these calculations give lower limits for the critical values of T_s and v.

I wish to express my thanks to D. A. Frank-Kamenetsky for valuable suggestions, to I. S. Roizen for his aid in carrying out the present work and to P. G. Sushchev for help in preparing the manuscript for the press.

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AN OSCILLOGRAPHIC INVESTIGATION OF THE OXIDES FORMED ON A NICKEL ANODE DURING THE ELECTROCHEMICAL EVOLUTION OF OXYGEN

Ya.I. Turyan and Yu.S. Gorodetsky

(Presented by Academician A.N. Frumkin, May 21, 1957)

For elucidating the mechanism of the oxygen overvoltage it is important to know the nature and the concentration of the oxides which are formed on a smooth nickel anode in an alkaline solution.

A number of authors have shown that oxygen is evolved on a nickel anode which is covered with 1-2 [1, 2], or with 5 [3] layers of Ni_2O_3 (β-NiOOH) [4-6]. According to certain other data [2, 4] a higher oxide, NiO_2, is also present on the anode. Despite the important role that this oxide plays in the electrochemical evolution of oxygen [3, 7], the extent of its formation on a smooth Ni anode is not known at the present time. In addition, the literature contains no information on the quantity of the oxides formed on the smooth Ni anode at high (industrial) current densities (≥ 0.1 amp/cm^2).

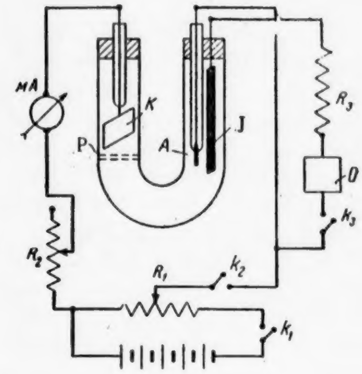

Fig. 1. Cell and electrical circuit.

We have developed a technique for the oscillographic investigation of the smooth Ni anode, through which it is possible to determine the amount of the stable oxide, and of the higher, unstable oxide as well. The essential feature of this technique is that the oscillator of the oscilloscope O (Figure 1) which was used for obtaining the discharge curve, was put into circuit with the test electrode before cutting out the polarizing current. The sensitivity of the oscillator was so chosen that its insertion into the circuit altered the strength of the polarizing current but little. After cutting off the polarizing current, a "complete" discharge curve was obtained which included the reduction of the higher, unstable oxide. In another experiment, the "incomplete" discharge curve corresponding to the reduction of the stable oxide was obtained by putting the oscillator into the circuit some time after cutting off the polarizing current. From the difference between the areas under the "complete" and the "incomplete" discharge curves the amount of the higher, unstable oxides was found.

This work was carried out with an 8-sweep oscilloscope of the MPO-2 type with a photorecorder. The test Ni anode A (Figure 1) of spectrally pure wire (3 electrodes were studied: $S_1 = 0.155$ cm^2, $S_2 = 0.21$ cm^2, $S_3 = 0.333$ cm^2) was discharged against a nonpolarized iron electrode, J, which had been taken from an ordinary alkali accumulator. Electrochemically purified 7.5 N KOH served as the electrolyte. The anode space was separated from the cathode region by a glass diaphragm, D. In order to give the Ni anode a stable surface, this electrode was initially subjected to the action of a pulsating current. The ratio of the true to the apparent surface, as subsequently determined by the alternating current method [8], was ~5.1. Since the potential of the iron electrode did not alter during the process of obtaining a discharge curve, the discharge potential of the Ni anode was determined from the known values of the resistance R_3 (which was taken to be many times greater than the internal resistance of the cell) and the discharge current. The potential determined in this manner was very close to that measured potentiometrically.

A time scale was obtained on the oscillographs with the aid of a 50-cycle alternating current. The density of the polarization current varied over the interval 0.1-2 amp/cm^2; that of the discharge current over 0.009-0.02 amp/cm^2.

During the time covered by a discharge curve the entire quantity of oxygen did not succeed in diffusing to the anode surface, due to the fact that rather thick oxide layers were formed on the electrode, especially in extended anodic polarization. Thus, for complete reduction of the oxygen it was necessary to obtain several other discharge curves after the first one, with a 3-5 minute time interval between exposures.

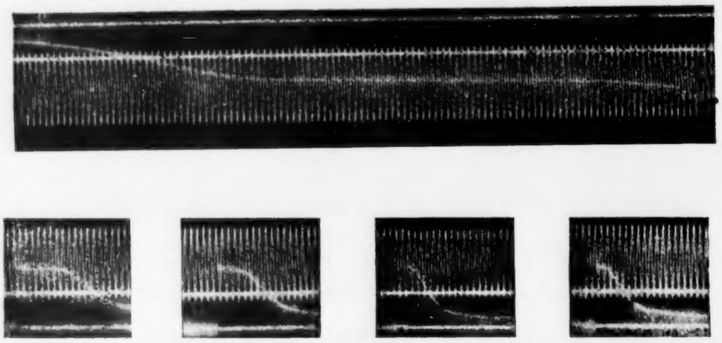

Fig. 2. "Complete" discharge curve.

In Figure 2 there is shown the general form of the "complete" discharge curves, both the initial one and those subsequent ones leading to the full reduction of the oxides. The upper horizontal segment on the first curve corresponds to the polarization current which was still flowing. The break point in the current comes at the instant of cutting off the polarizing current; there then follows an intermediate horizontal segment, after which the current falls to the lower horizontal level. In view of the fact that the discharging cell was essentially a micro alkali accumulator, the lower segment along which the current nearly falls to zero, corresponds to the presence of NiO on the anode surface. The intermediate horizontal segment is found at potentials ranging from +0.70 to +0.40 v (with respect to the normal hydrogen electrode) and corresponds to the reduction of NiO_2 and Ni_2O_3. In accord with other investigations [1,3], we did not note a separate area for the reduction of NiO_2, a fact which can be explained by the closeness of the potentials for NiO_2/NiO and Ni_2O_3/NiO. The current falls relatively slowly from the intermediate segment to the lower one, this being possibly related to the formation of intermediate oxides of the type Ni_3O_4 [2,4-6], although neither we nor other authors [1,3,9] have succeeded in detecting a corresponding area.

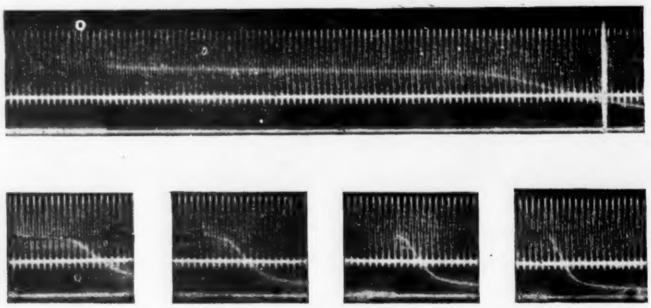

Fig. 3. "Incomplete" discharge curve.

The quantity of electricity corresponding to the "complete" discharge curve depended very weakly on the value of the polarizing current (over the interval of 0.1-2 amp/cm^2) but increased with an increase in the duration of polarization (in agreement with the data of [3]). Thus the area under the "complete" discharge curve was 7-8 mQ/cm^2 of true surface for a 5 minute polarization and increased to 11-12 mQ/cm^2 of true surface for a 30-60 minute polarization.

The "incomplete" discharge curve (Figure 3) did not have an upper horizontal segment since the polarizing current was cut off before the oscillator was put into the circuit. The area under the "incomplete" discharge curve was less than that for the "complete" discharge curve. This contraction in the area increased with the duration of the "relaxation" when the latter was very brief (several seconds), but beginning with 5-10 seconds "relaxation" and going up to several minutes, there was observed a rather constant contraction in the area of the order of 0.8-1 mQ/cm^2 of true surface. This value was practically independent of the density of the polarizing current (0.1-2 amp/cm^2) and the duration of polarization. By comparison with the complete discharge curve it was found that the contraction of the area occurred at potentials ranging from +0.70 to +0.60 v. This made it possible to explain the observed contraction in the area in terms of the autodecomposition of the higher oxide during the "relaxation" of the anode*:

$$2NiO_2 = Ni_2O_3 + \tfrac{1}{2}O_2. \qquad (1)$$

From the value of the contraction in the area it was found that the number of layers of NiO_2 was equal to ~3. This confirmed the conclusion drawn by one of us [7, 10], from indirect observations, that the surface of a Ni anode is fully covered with a higher oxide in the region of high current densities.

The amount of the stable oxide, Ni_2O_3, was found from the area of the "incomplete" discharge curve as obtained after a 20 second "relaxation," having first subtracted the Ni_2O_3 formed through Reaction (1). Even with a 5 minute polarization, this Ni_2O_3 amounted to ~17 layers and for a one hour polarization it was equal to ~30 layers. Thus, in the region of high current densities, a smooth nickel anode is covered with an oxide layer which is much thicker than that found in the experiments of [1-3] which were carried out at comparatively low densities.

The invariancy in the amount of the oxides under changing current density points to the possibility that the electrochemical evolution of oxygen does not occur solely through the formation and decomposition of oxides, this being in agreement with the indirect observations of other works [7, 11].

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*In the course of a prolonged "relaxation" (more than 5 minutes) there was observed in a number of experiments a further, nonreproducible contraction in the area under the "incomplete" discharge curve, which is clearly related to the reduction of Ni_2O_3 by impurities in the electrolyte.

** Original Russian pagination. See C.B. Translation.

THE ANTAGONISM OF IONS IN THE COAGULATION OF LYOPHOBIC SOLS BY ELECTROLYTES

Yu.M. Glazman, I.M. Dykman and E.A. Streltsova

(Presented by Academician P.A. Rebinder, June 10, 1957)

In a preceding paper [1] we have shown theoretically that synergism is to be observed over practically the entire range of concentrations during the coagulation of lyophobic sols by mixtures of two symmetric electrolytes of the $1-1+2-2$ type. At the same time the supposition was advanced that the theoretical conclusions could prove to be entirely different in the case of other electrolyte combinations; in particular, there was not to be excluded the possibility of the opposite effect, antagonism, on adding to a colloidal solution a mixture of electrolytes in which the positive ion of the first component (the one possessing the weaker coagulating action) of the pair was monovalent.

The present investigation was undertaken with a view to testing the correctness of this assumption. The calculations which we have carried out are analogous to the earlier ones [1] and have been extended to the case of the coagulation of a sol by a mixture of electrolytes of the type $1_2-2+2-2$, it being supposed that the first ion in each electrolyte is a coagulant and that the second carries a charge of the same sign as the colloidal particles.

Let it be supposed that unit volume of the solution contains n_1 positive ions and $2\,n_1$ negative ions of the first electrolyte, with the respective charges 2 *ez* and *ez*. In addition let this solution also contain n_2 positive and n_2 negative ions of the second electrolyte, each of charge 2*ez*. Just as in [1], we will assume that the colloidal particles of the sol whose stability is under investigation are sufficiently large in comparison with the effective dimensions of the ionic atmosphere so that two mutually interacting particles can be approximately represented as infinite parallel planes. We will designate the distance between these planes by *h* and the electrostatic potential at any point in the body of the solution by Ψ. The equation:

$$\frac{d^2\Psi}{dx^2}=\frac{8\pi e}{\varepsilon}\left[n_1\exp\left(\frac{ez\Psi}{\theta}\right)-n_1\exp\left(\frac{2ez\Psi}{\theta}\right)+2n_2\operatorname{sh}\left(\frac{2ez\Psi}{\theta}\right)\right], \tag{1}$$

which serves to determine Ψ is analogous to Equations (1) and (2) of [1]. Here the earlier symbolism has been retained: *e* is the elementary charge; *z* is the smallest of the valences of the ions in the given mixture; ϵ is the dielectric constant of the solution, and $\theta = kT$.

The first integral of Equation (1) determines the square of the field intensity. Repeating the reasoning and the calculations of [1], we write the expressions for the distance *h* and the force P acting on unit surface of the plane as:

$$h=\sqrt{\frac{\varepsilon\theta}{2\pi e^2}}\int\limits_{u_0}^{\infty}\frac{du}{[n_1(2u^3-2u^2u_0-u^2u_0^{-2}+1)+n_2(u^4-u^2u_0^2-u^2u_0^{-2}+1]^{1/2}}, \tag{2}$$

$$P=\theta\,[n_1(2e^{u_0}+e^{-u_0})+3n_2(\operatorname{ch}u_0-1)]. \tag{3}$$

For simplicity, in Expressions (2) and (3) the term Ψ has been replaced by the dimensionless potential u =

$= \exp(ez\,\Psi/\theta)$. It will be assumed that the potential on the plane surfaces (where $x = \pm h/2$) is positive and equal to u_1, whereas on the plane of symmetry ($x = 0$) it is equal to u_0. As earlier in [1], it will be supposed that the sol is strongly charged and, accordingly, that $u_1 \gg 1$. This justifies the infinite upper limit of the integral in (2).

For our problem it is essential that the entire range of possible concentrations, n_1 and n_2, is not of uniform interest. In the case of symmetric electrolytes, it was especially emphasized in the preceding paper [1] that it is only along the initial portion of the curve $n_{2C} = n_{2C}(n_{1C})$ that the effect exceeds that due to direct additivity. Even for the case of unsymmetrical electrolytes, which is under consideration here, it must be supposed that this same initial portion of the curve $n_{2C} = n_{2C}(n_{1C})$ is that which possesses the greatest interest. Thus, from the very outset it will be expedient to simplify the subsequent calculations by considering n_1 to be an infinitely small parameter and to everywhere retain only the linear members in developments in powers of n_1. To this approximation (and with $f = n_1/n_2$), the right-hand member of Equation (2) becomes the difference of two integrals

$$h = \sqrt{\frac{\varepsilon\theta}{2\pi e^2 n_2}}\left[I_1 - \frac{f}{2} I_2\right], \tag{4}$$

where

$$I_1 = \int\limits_{u_0}^{\infty} \frac{du}{(u^4 - u^2u_0^2 - u^2u_0^{-2} + 1)^{1/2}} = \frac{u_0}{u_0^2 + 1} K(k), \tag{5}$$

$$\begin{aligned} I_2 = \int\limits_{u_0}^{\infty} \frac{2u^3 - 2u^2u_0 - u^2u_0^{-2} + 1}{(u^4 - u^2u_0^2 - u^2u_0^{-2} + 1)^{3/2}} du = \\ = \frac{2u_0^4}{u_0^4 - 1}\left\{\frac{1}{u_0^2 + 1} F(\varphi, k) + \frac{1}{u_0^2 - 1}[E(\varphi, k) - 1]\right\} + \\ + \frac{u_0}{u_0^4 - 1}\left[\frac{u_0^4 - 2u_0^3 - 1}{2(u_0^2 + 1)} K(k) - \frac{u_0^4 - 2u_0^3 - 1}{2(u_0^2 - 1)} E(k) - \frac{2u_0}{u_0^4 - 1}\right]. \end{aligned} \tag{6}$$

Here $K(k)$ and $E(k)$ are, respectively, complete elliptic integrals of the first and second kinds and $F(\varphi,k)$ and $E(\varphi,k)$, incomplete integrals of the first and second kinds. The argument φ and the modulus $\underline{k}$ are determined by the relations:

$$\varphi = \arctan\left(\frac{u_0^2 + 1}{u_0^2 - 1}\right)^{1/2}, \qquad k = \frac{2u_0}{u_0^2 + 1}. \tag{7}$$

For fixing the "critical" value h_C and the "critical" concentrations, n_{2C} and n_{1C}, we will make use of the Deryagin-Landau equation [2] $(h/P)(dP/dh) = -3$, which, in our case, can be conveniently written as

$$h\frac{dP}{du_0} = -3P\frac{dh}{du_0}. \tag{8}$$

By introducing the Expressions (2, 3) into Equation (8), and taking (4-7) into account, we obtain an equation whose root directly determines the "critical" value u_0. This equation has the form:

$$\frac{3}{2}E(k) - K(k) = f\Phi(u_0), \tag{9}$$

where $\Phi(u_0)$ is a function of u_0 which is not presented here because of its complexity. Equation (9) goes over into the well-known Deryagin-Landau equation [2] when $f = 0$:

$$\frac{3}{2}E(k) - K(k) = 0. \tag{10}$$

The root, k_0, of Equation (10) is equal to 0.77394. According to Equation (7), this corresponds to the value $u_{00} =$ $= 2.1103$.

When f is different from zero, a solution for Equation (9) can be sought in the form

$$u_0 = u_{00} + u_{01}. \tag{11}$$

Setting (11) in Equation (9), taking into account the fact that u_{00} satisfies Equation (10), making certain simple rearrangements and retaining only expressions which are linear with respect to f, there is obtained an equation of the type:

$$\left[-\frac{u_{00}^2-1}{2u_{00}(u_{00}^2+1)}K(k_0)+\frac{u_{00}^4-10u_{00}^2+1}{2u_{00}(u_{00}^4-1)}E(k_0)\right]u_{01}=f\Phi(u_{00}). \tag{12}$$

for the determination of u_{01}. From this it follows that $u_{01} = 0.1379f$. Thus, with an accuracy corresponding to components linear in f, the complete expression for the root of Equation (9) is:

$$u_0 = 2.1103 + 0.1379f. \tag{13}$$

According to Equations (2) and (3), when u_0 is given by (13), the calculated values of the "critical" distance, h_c, and the "critical" force, P_c, are equal to:

$$h_c = \sqrt{\frac{\varepsilon\theta}{2\pi e^2 n_2}}\,(0.7540 - 0.1765\,f), \tag{14}$$

$$P_c = n_2\theta\,(2.678 + 1.998\,f). \tag{15}$$

If the repulsive force, P_c, and the force, Q, of mutual molecular attraction between plane colloidal particles, separated from one another by a distance h_c:

$$Q = \frac{\pi A}{6h_c^3}, \tag{16}$$

(A is the constant of molecular attraction) are now equated, we are led, just as in [1, 2], to an equation of the type:

$$\alpha + \beta f = B\sqrt{n_{2c}}, \tag{17}$$

from which the "critical" concentration, n_{2c}, of the second electrolyte can easily be found. According to Equations (14-16), the constants which enter into Equation (17) have the values:

$$\alpha = 1.148; \quad \beta = 0.05053; \quad \beta = \frac{\pi^2 A e^3}{3\varepsilon\theta^2}\sqrt{\frac{2\pi}{\varepsilon\theta}}. \tag{18}$$

Finally we find

$$n_{2c} = \frac{1}{B^2}(\alpha^2 + 2\alpha\beta f); \quad n_{1c} = \frac{\alpha^2}{B^2}f. \tag{19}$$

At the point $n_{1c} = 0$, the derivative dn_{2c}/dn_{1c} is equal to:

$$\frac{dn_{2c}}{dn_{1c}} = \frac{2\beta}{\alpha} = 0.088. \tag{20}$$

The positive sign of this derivative dn_{2c}/dn_{1c} indicates that antagonism must be observed during the coagulation of a sol with a mixture of two electrolytes of the $1_2 - 2 + 2 - 2$ type.

Thus, the theory shows that coagulation of lyophobic sols with mixtures of electrolytes of the $1-1+2-2$ type is qualitatively opposed to the coagulation obtained with mixtures of the $1_2-2+2-2$ type; in the first case synergism is theoretically indicated, whereas the second leads to a clearly expressed antagonism.

The results which have been obtained can be interpreted in terms of the Pauli theory [3] of the "effect of discharge" of colloidal particles which is known to depend on the electrostatic effect of the secondary ions of the coagulating electrolytes. At the same time, the theoretical results are qualitatively supported by certain direct measurements which we have carried out. Thus, for example, a clearly expressed synergism is observed in the coagulation of a hydro-sol of rosin by mixtures of the electrolytes $KCl + MgSO_4$, and it is only at the very beginning of the curve (at small concentrations of KCl) that the effect is insignificantly greater than that due to direct additivity. On the other hand, the phenomenon of antagonism is observed on coagulating this same sol with $K_2SO_4 + MgSO_4$ mixtures, this being expressed in a rather high degree, so that for all ratios of these electrolytes the curve lies above that of direct additivity.

The entire mass of literature referring to the problem of coagulation of lyophobic sols by mixtures of electrolytes indicates, just as does our own data on this problem, that this antagonism is not uniform in various cases. It is clear that two types of antagonism exist in the coagulation of lyophobic colloids: 1) an antagonism between the coagulating ions, which is related to the competition for adsorption positions on the surfaces of the colloidal particles, and 2) an antagonism which results from the mutual electrostatic action of ions in the body of the solution and in the electrical field of the colloidal particles.

The authors wish to take this opportunity to express their thanks to B.V. Deryagin for the interest which he has shown in this work and for a very fruitful discussion of the results.

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THE SHEAR STRENGTH OF TWO-SIDED FILMS AND SURFACE LAYERS IN SAPONIN SOLUTIONS

K.V. Zotova and A.A. Trapeznikov

(Presented by Academician P.A. Rebinder, June 11, 1957)

The structures, compositions and properties of adsorption layers of solutions of saponin and detergents are of much interest for colloidal chemistry and the same is true of the two-sided films which are formed from these solutions and which appear as the elements of foam networks.

In the preceding papers of one of the present authors [1], a technique was developed for investigating the mechanical properties of films and surface layers in soap solutions;also,saponin films were subjected to certain preliminary measurements. It is customary to assume identical structures and compositions in an adsorbed surface layer on a solution of a surface-active substance and in a two-sided film which has been formed from this same solution. As has been shown in [2], this may not be justified. This point is of much significance for understanding many of the peculiarities of the properties of films and foams and especially the relation between stability and concentration.

The simultaneous investigation of the mechanical properties of two-sided films and surface layers at various concentrations represents a new method for studying film characteristics and compositions.

In this work a method has been applied which permits the measurement of the shear strength of surface layers and two-sided films [3]. Two concentric rings of platinum wire, 0.1 cm in diameter, with radii $R_1 =$ $= 2.738$ cm and $R_2 = 2.995$ cm, were arranged horizontally. The external ring was firmly fixed to the walls of a cup which through a communicating tube could be filled from below with the solution contained in a leveling bulb,the inner ring being hung on an elastic tungsten filament, $d = 0.01$ cm, $l = 27.0$ cm, which had an elastic constant of 53.6 dyne · cm/radian. This entire system was enclosed under a hermetically sealed glass bell resting on a table and was immersed in an air thermostat.

In this procedure, either the level of the saponin solution in the cup was raised to the exact center of the rings, locating the latter in the solution surface layer, or the solution was first raised above the rings and then lowered somewhat beneath them, a two-sided film being formed between the rings and then torn loose from the solution.

By turning the inner ring, a deformation was set up in the solution surface layer or in the narrow two-sided film between the two platinum rings as the case might be. Depending on the magnitude of the resistance of the system under investigation and on the parameters of the apparatus, the inner ring experienced various types of movement (torsional-vibration, aperiodic or progressive displacement) as the result of imposing constant or continuously (stepwise) increasing loads (twist angles of the filament). The last of these types of movement gave deformation vs. load curves which corresponded to the various mean rates of loading.

Any successful method for measuring the mechanical properties must be sufficiently rapid. For films possessing shear resistance, the most satisfactory technique is that of stepwise loading, since this makes it possible to obtain curves of deformation, ϵ, vs. shear stress, P, from which there can be found the limit of the structural stability, P_r, which corresponds to the given conditions of deformation (increments in P in an amount 0.072 dyne/cm were imposed periodically at 15 second intervals).

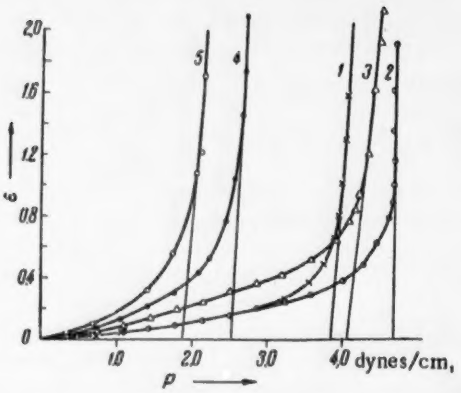

Fig. 1. Curves of the ϵ vs. P relations for two-sided films formed from saponin solutions of various concentrations: 1) 0.05%; 2) 0.1%; 3) 0.2%; 4) 0.5%; 5) 1%.

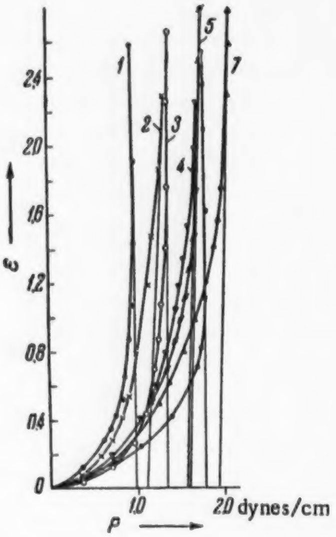

Fig. 2. Curves showing the ϵ vs. P relations for surface layers in saponin solutions: 1) 0.005%; 2) 0.01%; 3) 0.05%; 4) 0.1%; 5) 0.2%; 6) 0.5%; 7) 1%.

We have investigated various saponins which, as it turned out, differed radically in their ability to form films and foams and in their mechanical properties as well. Imported saponins from manufacturers of pure chemical reagents were studied together with domestic preparations from various plants. Here there will be considered the data on one of the imported saponins (Kahlbaum) which, under the working conditions, formed comparatively stable films of high mechanical strength between the rings.

In Figure 1 there are presented curves showing the ϵ vs. P relations for two-sided films which were formed from solutions of various concentrations, C. Here $\epsilon = 2\theta R_2^2/(R_2^2 - R_1^2)$ and $P = C_0(\varphi - \theta)/2\pi R_1^2$, where θ is the displacement of the inner ring, φ is the twist angle of the upper end of the filament, and C_0 is elastic constant of the latter.

From these curves it is to be seen that ϵ increases especially rapidly when P reaches a certain value, $P = P_r$ (which is found by extrapolation to the axis of abscissas, but which could be more exactly determined from the maximum on the P vs. ϵ curve [4]), this fact pointing to the initiation of the flow which is associated with structural breakdown.

In Figure 2 there are presented curves showing the ϵ vs. P relations for surface layers in these same saponin solutions. In general, these are similar to the curves for the films, but differ from the latter in the fact that there is a more gradual transition to the vertical segment which reflects the structural breakdown and flow. Due to their instability it was not possible to determine the shear strengths of films for which $C < 0.05\%$. For surface layers, data were obtained for solutions at concentrations down to $C = 0.001\%$.

In Figure 3 curves are given to show the P_r vs. C relations for two-sided films and for solution surface layers, measurements having been made in each case both on fresh solutions and solutions which had been aged for 3 days.

In conformity with the data of other authors [5], the value of P_r increases with the concentration in the case of newly prepared surface layers of fresh solutions but in the case of two-sided films from the same solutions, Figures 1-3 show that P_r passes through a sharp maximum in the region of comparatively low concentrations ($C = 0.1\%$). In essence, this effect is retained for films which have been formed from aged solutions, but there is an increase in the structural strength. A clear-cut maximum in the interval of small concentrations (at $C = 0.005\%$) also appears with surface layers which are formed from aged solutions.

The difference between the values of P_r for films and for solution surface layers indicates that at small C's, where the P_r value of the film is 3-4 times greater than that of the surface (the number of adsorbed layers in the film being only twice greater than in the surface), there are predominantly transferred into the film those components which give to it a higher shear strength. This selectivity of transfer of the various components into the film is also confirmed by the form of the P(ϵ) curves. At small values of C, the P(ϵ) curves for the films pass more abruptly into the region of flow which is associated with the structural breakdown (Figure 2).

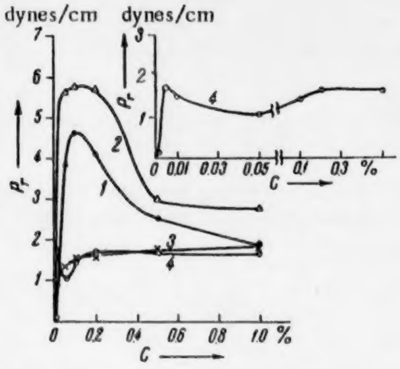

Fig. 3. Curves showing the P_r vs. C relations for two-sided films (1 and 2) and for surface layers (3 and 4). 1 and 3 are for freshly prepared solutions; 2 and 4, for solutions which had been aged 3 days.

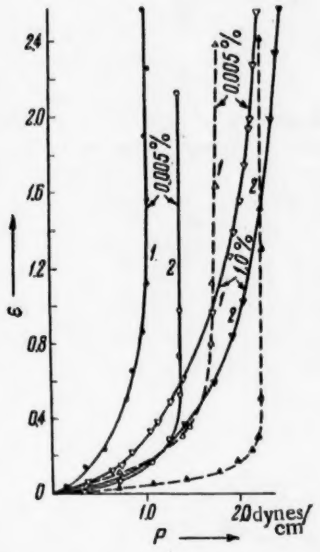

Fig. 4. Curves showing the ε vs. P relations for surface films of saponin solutions of various concentrations: 1) in the surface layer 2-3 minutes after its formation; 2) in this same layer aged for 20 minutes after completing the preceding measurement. The full curves are for freshly prepared solutions, the dotted curves, for solutions which had been aged 3 days.

The decrease in the P_r value of the film down to the P_r values for the surface which occurs with increasing C, shows that the strength of the adsorption layer in the film is only half that of the adsorption layer in the surface, i.e., there now predominates the transfer of less "rugged" components into the film. This shows that in the concentrated solutions, the "rugged," more active components are more tightly bound to the less rugged components. It is possible that the latter are more hydrophylic and solubilize the less hydrophilic, more active components. At low solution concentrations, a dissociation of these components is possible and the more active among them, being, in an isolated condition, more readily selectively transfer into the film. On aging a saponin solution, the more active components are clearly aggregated as the result of hydrolytic cleavage, the stability of the film being thereby increased and its shear strength raised. The existence of such a process is confirmed by the greater fragility of the surface layers which are formed from aged solutions, particularly in the case where the layers themselves have been given an additional 20 minute aging (Figure 4). This aging of the layers themselves is of great significance for solutions of low concentrations, C, in which an aggregation of the more active "rugged" components is possible. It is frequently considered that micells are not present in saponin solutions. In actuality micells similar to those which are formed in soap solutions are in all likelihood not present here. Nevertheless, the effect of solubilization is not thereby excluded. There is no doubt that even in carefully purified saponin, and especially in the commercial product, there are components of varying surface activity which also differ in molecular structures and the effects of solubilization or dissociation of complexes in saponin solutions must accordingly be considered as completely possible.

In the above experiments the mid-portion of a two-sided film was clearly not significant in fixing the over-all mechanical properties. Nevertheless, cases are observed in which the mechanical properties and the structure of the mid-portion of the film play a greater role in comparison with the adsorption layers. Thus, if from aged solutions of cyclamen and gladiolus saponins,several two-sided films are successively formed, it is found that the viscosity continuously diminishes. For example, with solutions of cyclamen at C = 0.5%, the viscosity diminishes from 1.3 to 0.016 surface poises on passing from film No. 1 to film No. 12. On relaxing the solution, the film viscosity again increases, tending to the original value. This effect can be explained by the transfer into the central part of the film of the structure which is formed in the body of the solution. Such structure can thixotropically collapse in the body of the solution during the inevitable mixing which results from the sequential formation of the films and be regenerated during relaxation, thereby influencing both the structure and the mechanical properties of the film.

It is interesting to note that the decrease in the viscosity of the successively formed films is accompanied by a diminution of their stability as well (from 18 to 2 minutes). Thus, in this case a parallelism is observed between the mechanical properties of the films and their stability between the rings. It is impossible to affirm, however, that such parallelism is to be met, in all cases, and that the mechanical properties completely determine the stability of films and foams.

It must be kept in view that in none of the enumerated cases are the adsorption layers in films and on solution surfaces at equilibrium.

The differences between the properties and compositions of the adsorption layers in two-sided films and in surface layers which have been considered here make possible the elucidation of many of the details of the stability of foams as well as the results of investigations of the mechanical properties of adsorption layers which have been carried out by various authors.

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THE KINETICS AND MECHANISM OF THE HOMOGENEOUS GRAPHITIZATION OF CARBON

V.I. Kasatochkin and A.T. Kaverov

(Presented by Academician A.A. Skochinsky, July 13, 1957)

The homogeneous graphitization of carbon (2000-2800°) is characterized by a continual perfection of the three-dimensional order in the graphite crystal lattice, this being the result of azimuthal orientation of the parallel basic lattices in packets which were formed in the "pre-crystallization" stage [1, 2]. According to x-ray data, the coexistence of amorphous and crystalline phases is not to be observed during homogeneous graphitization and this should, accordingly, be considered as an orientation process resembling the formation of an oriented polymer insofar as there is no accompanying phase transformation [3]. In the present work there are presented the results of an x-ray study of the kinetics and mechanism of the isothermal graphitization at 2000, 2150, 2300, 2420 and 2800° of cokes from cracking and from oil pyrolysis. Graphitization was carried out in an atmosphere of nitrogen and argon in a furnace equipped with graphite heaters. The maximum deviation of the temperature from its pre-determined value amounted to ± 25°. Depending on the duration of isothermal treatment in the furnace, (hkl) bands of continually increasing sharpness and intensity appeared on the x-ray diagrams (Figure 1). The half widths of the (hkl) and (001) bands also diminished. These changes in the x-ray diagram reflect the azimuthal orientation of the packets of parallel carbon lattice planes with the initiation and further perfection of the three-dimensional order.

In addition, there was observed a regular diminution of the interplanar spacing d_{002} (Figure 2), this also being related to the azimuthal orientation of the carbon layers into a more dense packing. The existence of a direct relation between d_{002} and the three-dimensional ordering of the carbon is indicated by character of the changes in the x-ray diagram and this, in turn, justifies the introduction of a measure of this ordering in terms of Δd, the decrease in the interplanar spacing, such as is defined by the relation

$$\gamma = \frac{\Delta d}{\Delta_0} = \frac{3.425 - d_{002}}{0.069}, \quad (1)$$

Δ_0 being the entire interval for the change in d_{002} during the transition from ungraphitized carbon, with the value $d_{\mathrm{ungr}} = 3.425$ A, over to maximally graphitized carbon with the minimum value, $d_{\min} = 3.356$ A.

This quantity, γ, is of statistical character; it determines the probability of simultaneously depositing neighboring carbon monolayers on both sides of a given layer so as to form a stratum of elementary cells and is related to the earlier introduced probability, u (4,1), for the oriented arrangement of two neighboring monolayers of carbon.

The dependence of the x-ray density on d_{002} is determined from the volume, ω, and the mass, M, of the elementary cell by

$$\rho = \frac{M}{\omega} = \frac{7.627}{d_{002}}, \quad (2)$$

d_{002} being in A and ρ, in g/cm^3. By eliminating d_{002} from (1) and (2), the relationship between the x-ray density and the degree of order, γ is obtained (Figure 3). The curve showing the dependence of the ratio of the integral

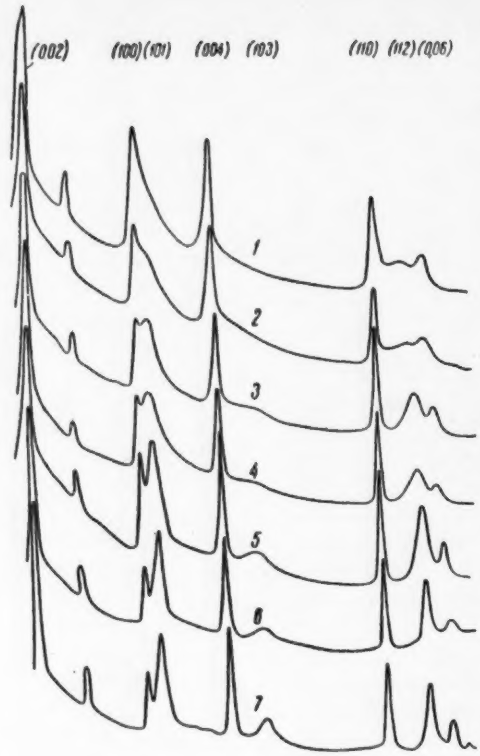

Fig. 1. Microphotograms of cracking coke which had been held at certain temperatures over various periods of time: 1) 2000°, 13 hours; 2-6) 2300° isotherms for the heating periods: 2) ½ hour; 3) 1 hour; 4) 1½ hours; 5) 3 hours; 6) 4 hours; 7) 2800°, ½ hour.

intensities I_{112}/I_{110}, on γ (Figure 3) in specimens obtained from treatments of varying duration at different temperatures is suitable for the practical determination of the degree of graphitization [2]. Direct graphing of $\log(1-\gamma)$ vs. τ relation (Figure 4) shows that the degree of three-dimensional ordering of carbon depends on the duration of isothermal treatment through the monomolecular kinetic equation

$$\gamma = 1 - e^{-K\tau}, \tag{3}$$

correction having been made for temperature variations at the beginning of the heating period. In Table 1 there are presented velocity constants for isothermal graphitization at various temperatures.

TABLE 1

T°K	$K \cdot 10^4$ (sec^{-1})	
	cracking coke	pyrolysis coke
2273	0.083	0.080
2423	0.441	0.417
2573	1.042	1.031
2693	2.246	2.460

For both cokes the mean, experimentally determined value of the energy of activation is about the same and is equal to $A = 92 \pm 5$ kcal/g-at.

This comparatively high value for the energy of activation indicates that the kinetics of graphitization is determined by a chemical process. The experimental energy of activation proves to be considerably less than the energy of rupture of the bond between the atoms in

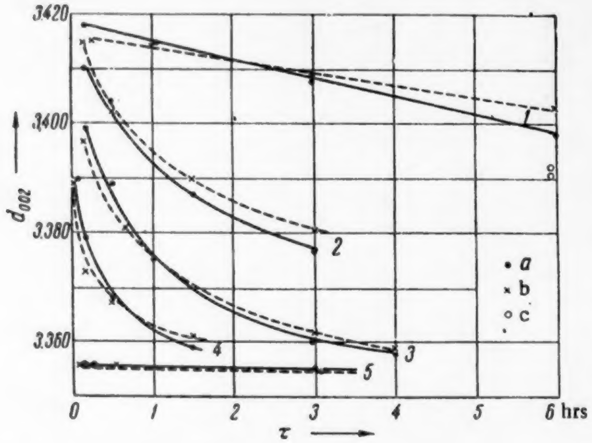

Fig. 2. The diminution of the interplanar spacing d_{002} and its dependence on the time of treatment at various temperatures. The accuracy of determination of d_{002}, ± 0.002 A: 1) 2000°; 2) 2150°; 3) 2300°; 4) 2420°; 5) 2800°; a) cracking coke; b) pyrolysis coke; c) points corresponding to treatment at 2000° for 13 hours.

the basic carbon lattice planes (~170 kcal/g-at.).This serves as an independent confirmation of the orientation mechanism of homogeneous graphitization. For the so-called nongraphitizing carboniferous materials, at higher temperatures there can be postulated a recrystallization mechanism with an accompanying reorganization of the carbon lattice. The high energy barrier for the orientation process should be related to the rupture of the short bonds between the carbon atoms of the lateral radicals, these giving rise to binding between the basic carbon lattices of neighboring "crystallites." In all likelihood the carbon atoms which enter into the makeup of these lateral radicals differ in valence from the carbons of the basic lattice. It can be supposed that they exist in one of the three possible states of s-p hybridization of the electronic orbits, two σ-bonds being at an angle of 180° and two π-bonds perpendicular to the carbon chain. It should be pointed out that it is the presence of strong lateral bonds between the carbon layers of neighboring "crystallites" which determines the high polymer nature of graphitized carboniferous materials and the associated peculiarities in their properties.

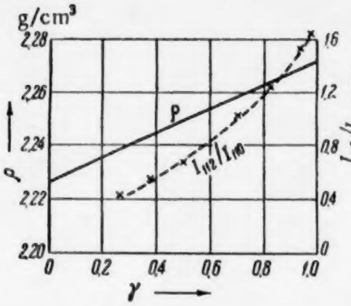

Fig. 3. The dependence of the x-ray density, and the ratio of the integral intensities I_{112}/I_{110}, on the degree of order.

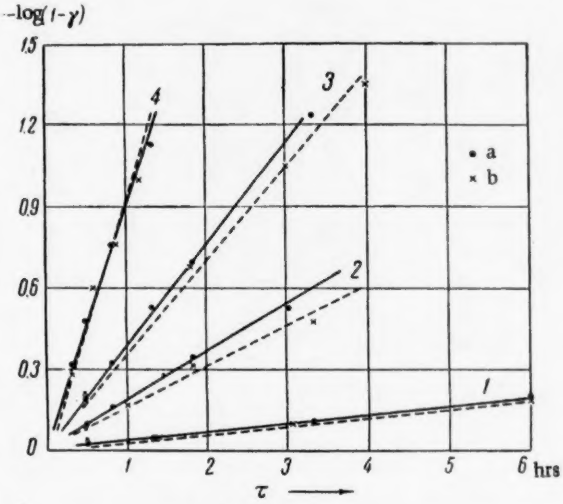

Fig. 4. The relation between the temperature and the velocity constant, K, for isothermal graphitization: 1) 2000°; 2) 2150°; 3) 2300°; 4) 2420°; a) cracking coke; b) pyrolysis coke.

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THE DETERMINATION OF THE DEGREE OF SUPERSATURATION IN THE AQUEOUS MEDIUM OF SUSPENSIONS OF TRICALCIUM ALUMINATE AND THE KINETICS OF ITS CHANGE

E.E. Segalova, E.S. Solovyeva and Academician P.A. Rebinder

The supersaturation which arises in suspensions of mineral binders is of decisive significance for the processes of crystallizational structure formation (solidification), earlier papers from our laboratory [1-3] having shown that the magnitude and the duration of this supersaturation essentially determine those conditions which are required for the appearance of crystallization contacts.

Measurements of the degree of supersaturation of suspensions of individual binders have been reported in the literature, but only for the hemihydrate of gypsum has there been established the maximum degree of stable supersaturation, a quantity which can be provisionally considered as the "solubility" of the gypsum hemihydrate [4]. Data are available which point to the formation of supersaturated solutions in suspensions of the individual minerals from alumina and portland cement clinkers [5], but systematic investigations of the magnitude of this supersaturation and the kinetics of its change are lacking.

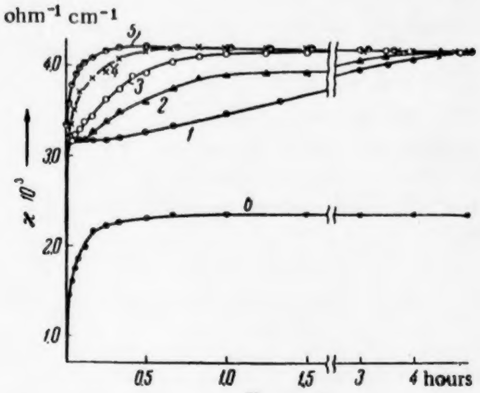

Fig. 1. The kinetics of the specific electrical conductivity in suspensions containing per 150 ml of water: 1) 1.0 g C_3A; 2) 1.5 g C_3A; 3) 2.0 g C_3A; 4) 4.0 g C_3A; 5) 6.0 g C_3A; 6) 4.0 g of the hydrate of C_3A.

The present work aimed at carrying out such an investigation on those suspensions of tricalcium aluminate (C_3A), whose structure formation we had studied earlier in detail [3]. Measurements of the kinetics of supersaturation in these C_3A suspensions were performed at an optimal rate of agitation (400 vib/min) [2, 6] using a conductrimetric method. In order to protect the suspensions from carbonation, all measurements were carried out in an atmosphere of nitrogen.

In Figure 1 there is shown the change in the specific conductivity of C_3A suspensions of various concentrations at 20°. It is, first of all, necessary to note that a fixed level of conductivity corresponding to a maximum degree of supersaturation is established in each of the concentrated suspensions, this being a quantity which could be provisionally considered as a kind of "solubility" of the initial compound, i.e., the anhydrous binder.

In distinction from the suspensions of the hemihydrate of gypsum in which the level of maximum conductivity was reached almost instantaneously (20-30 seconds), a constant level of supersaturation is built up comparatively slowly in the C_3A suspensions and the rate of its attainment sharply increases with an increase in the suspension concentration. At low concentrations of the suspension it is easy to distinguish two segments on the kinetic curves for the conductivity. Initially the conductivity increases very rapidly, but at $\varkappa = 3.2 \cdot 10^{-3}$ ohm^{-1} cm^{-1} there is observed a break followed by a gradually sloping section which is the more sharply developed the lower the concentration of the dispersed solid phase in the suspension. Beyond this break, the conductivity increases much more slowly than before. The instant corresponding to the break in the curve is associated with the appearance in the suspension of newly-formed, minute crystals of hydroaluminate as is clearly revealed by the pronounced turbidity of the dilute suspension.

The kinetics which have just been described can be interpreted in the following manner. On being brought into contact with water, C_3A begins to rapidly dissolve but, in distinction to the suspensions of the hemihydrate of gypsum, even at supersaturations far removed from the maximum, nuclei of a new phase, the microcrystallites of hydroaluminate, begin to appear in the suspension. These microcrystallites settle out on the surface of the initial C_3A particles, covering them, as it were, by a protective film and retarding their further dissolving. The diminished rate of increase of the electrical conductivity is related both to the retardation of dissolving and to the fact that a part of the material which passes into solution separates out in the form of the hydroaluminate without increasing the supersaturation of the solution.

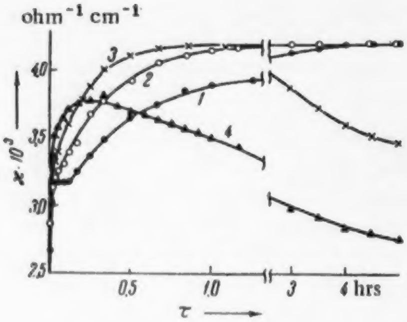

Fig. 2. The kinetics of the specific conductivity of suspensions containing 1.5 g C_3A in 150 ml of water with addition of hydroaluminate to the extent of: 1) 0 g; 2) 0.5 g; 3) 2 g; 4) 6 g.

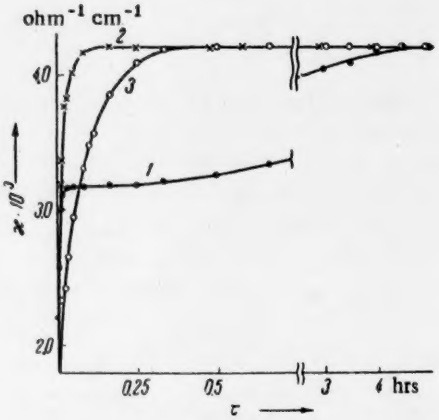

Fig. 3. The kinetics of the specific conductivity of suspensions containing 1 g C_3A in 150 ml of water or of asr solution: 1) water; 2) 0.05% solution asr; 3) 0.5% solution asr.

The hypothesis of the appearance of a protective envelope of new formations on the surface of the C_3A particles can be expediently tested as follows:

1) By the introduction of crystallites of previously prepared hydroaluminate into a C_3A suspension, those conditions should result under which the probability of the formation of new hydroaluminate nuclei would be strongly depressed, the material which passes into solution crystallizing out on the crystallites of the hydroaluminate which are already present in it.

2) By the introduction of small amounts of a surface active substance which would absorb on the initial C_3A particles, there should be, on the one hand, a retardation of the dissolving and, on the other, a preclusion to the settling out of the microcrystallites of the hydroaluminate on the surface of the particles, these being already covered by an absorbed layer of additive.

In Figure 2 there is shown the kinetics of the conductivity in C_3A suspensions containing various amounts of prepared hydroaluminate; Figure 3 gives the kinetics in the presence of small additions of alcoholic sulfite residue (asr).

As is to be seen from Figure 2, additions of the hydroaluminate markedly increase the rate at which the solution concentration rises.

Since the rate of dissolving of the C_3A cannot be increased by the presence of the hydroaluminate and the rise in the electrical conductivity should be retarded as a result of increasing the rate of crystallization of the hydroaluminate on the preexisting centers, the accelerated saturation of the solution can only be explained by the fact that in the presence of the hydroaluminate there is not formed that coating of crystallites which blocks the surface of the initial C_3A particles and as a result there is no retardation of the latter's dissolving.

The larger the addition of the hydroaluminate, the less the likelihood of the formation of the microcrystallites on the surface of the initial C_3A particles and the greater the rate of dissolving of the latter. With an increase in the amount of additive there is an associated increase in the rate of crystallization so that with large amounts of the hydroaluminate the upper limit of supersaturation is not reached (Figure 2, 4).

It is to be seen from Figure 3 that small additions of asr which are completely absorbed by the initial C_3A particles [3] do not change the maximum level of the conductivity but essentially affect the kinetics of the process: with 0.5% asr there is a pronounced diminution in the initial rate of dissolving of C_3A up to the appearance of nuclei of the new phase. However, with asr, just as with the hydroaluminate, no break is to be observed in the curve showing the increase of the conductivity and the maximum value of the conductivity is reached much more rapidly with the additive than without it.

With large additions of asr, the retarding influence of the latter on the initial rate of dissolving of C_3A becomes more pronounced but as a result of the presence of the asr in the liquid phase of the suspension, the value of the conductivity is so altered that the data obtained are incompatible with the preceding measurements.

These results can only be explained by the fact that the prevention of the formation of a protective hydroaluminate film on the surface of the initial C_3A particles proves the predominant effect despite a certain retardation of the dissolving due to the absorption of asr. As a result, the rate of saturation of the solution is markedly increased in the presence of small additions of asr.

To determine the magnitude of the maximum degree of stable supersaturation in C_3A suspensions, it was necessary to separate the liquid phase and determine its content of CaO and Al_2O_3.

Attempts at filtering or centrifuging the C_3A suspension after maximum supersaturation was reached did not give positive results. The crystallites of hydroaluminate which arise are so small that they practically do not settle in the common centrifuge and block the pores of the filter during filtration; the liquid filters so slowly that the supersaturation in it is reduced to zero.

It is known [3] that coarser crystals of the hydroaluminate form in the presence of small additions of asr, the magnitude of the maximum supersaturation remaining unaltered. For this reason the determination of the maximum supersaturation was carried out in suspensions containing very small additions of asr (0.01-0.05% asr in solution).

In this manner there was successfully determined for the first time the maximum degree of stable supersaturation in C_3A suspensions. At 20° it proved to be equal to 1.428 g C_3A/l of solution, this corresponding to the concentrations: CaO, 0.888 g/l and Al_2O_3, 0.540 g/l; $CaO : Al_2O_3 = 2.99$. The determinations of CaO and Al_2O_3 were performed gravimetrically. The values which have been presented represent the mean of 7 determinations. The solubility of the hydroaluminate as determined by this same method both in pure water and in weak asr solutions proved to be equal to 0.412 g/l of CaO and 0.260 g/l of Al_2O_3, these values being in good agreement with data of the literature [7].

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THE DEPENDENCE OF THE RATE OF HYDROGENATION ON THE AMOUNT OF RANEY NICKEL CATALYST

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A number of investigations [1-4] have shown that the rate of hydrogenation in the liquid phase is proportional to the mass of the catalyst when the amount of this latter is small, and tends to a limiting value when this amount becomes large. According to certain authors [5, 6], the more involved relationships which have been observed are tied up with the very low intensities of agitation of the reacting mixtures.

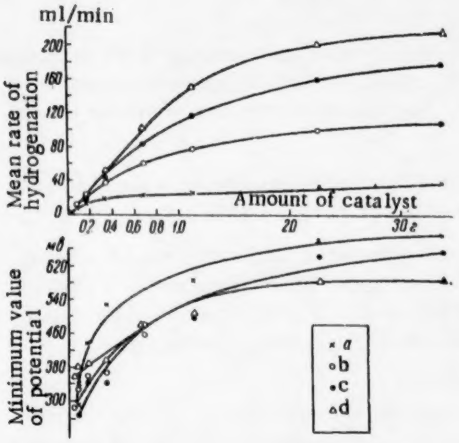

Fig. 1. The dependence of the rate of hydrogenation of hexine-1, and of the minimum value of the catalyst potential during reaction, on the amount of Raney nickel catalyst. Amount of hexine-1, 0.5728g; temperature, 20°; solvent, absolute alcohol. a) 250; b) 450; c) 650; d) 850, vib/min.

The purpose of the present investigation was to study this problem under ideal conditions, application being made of the potentiometric method through which it is possible to judge as to the processes occurring on the catalyst surface. The hydrocarbons hexine-1 and trans-piperine were chosen as test materials. The experimental technique was that which has been described in [7].

Hexine-1 was hydrogenated in absolute ethanol and in n-heptane, the nonpolar properties of the latter assuring that the process proceeded under ideal conditions.

It is to be seen from Figure 1 that the linear portion of the curve expressing the dependence of the rate of hydrogenation in alcohol on the amount of Ni increases in length with increasing intensity of agitation. For experiments in this medium, the kinetic curves are of approximately zero order. The difference in potential of the catalyst with respect to the reversible hydrogen electrode varies from 50 mv (3.384 g Ni) to 360 mv (0.034 g Ni).

In n-heptane the observed behavior is somewhat different. In the region of small amounts of catalysts, the rate of hydrogenation is proportional to the amount of Ni to a power in excess of the first. The specific activity of the catalyst passes through a maximum, which, with increasing intensity of agitation, is displaced in the direction of larger charges of Ni. It must be noted that with small amounts of Ni, the rate of hydrogenation in n-heptane is lower than in alcohol, whereas with larger amounts it is considerably greater.

In the course of the hydrogenation of trans-piperine in alcohol there is taken up only 70% of the theoretically required amount of hydrogen, this being due, in all likelihood, to the occurrence of simultaneous side reactions. These kinetic curves are of an order close to the first; the potential of the catalyst varies over the same range as in the case of hexine-1 and the specific activity passes through a maximum.

In series of experiments the hydrogenation of hexine-1 in alcohol was studied at a fixed value of the ratio, amount of unsaturated compound to amount of catalyst (0.38 hexine-1 per 1 g Ni). These experiments were carried out at 250, 450, 650 and 850 vibrations of the flask per minute and at temperatures of 2, 20 and 40°. The amount of catalyst was varied from 0.084 to 3.384 g.

With weak agitation, the specific catalytic activity diminishes with an increase in the amount of the catalyst and with strong agitation it passes through a maximum. It should be emphasized that a maximum specific activity is observed (see Table 1) at a quite definite value of the catalyst potential, i.e., at a fixed degree of coverage of the active surface by the reacting molecules.

TABLE 1

Intensity of agitation, vib/min	Temperature, °C	Charge of Ni for which the specific activity is a maximum, g	Mean absolute potential of catalyst, mv	Specific activity, ml/min · g
450	2	0.338	610	71
650	2	0.338	620	93
850	2	0.676	690	113
850	20	0.676	675	137
850	40	0.338	685	252

With an increase in the intensity of agitation, there is a diminution in the concentration of the unsaturated compound on the catalyst surface. By varying the temperature, the coverage of the surface by the unsaturated compound is left unchanged but the maximum specific activity is displaced in the direction of smaller charges of Ni.

The apparent energy of activation is a function of the absolute value of the ratio between the charge of material and the quantity of catalyst and varies from 1.5 kcal/mole (3.384 g Ni) to 8 kcal/mole (0.084 g Ni).

With a view to elucidating the intermediate stages in the hydrogenation of hexine-1, a number of experiments were interrupted after the absorption of a definite volume of hydrogen; following the method of Barnes and Molinini [8] the flask contents were analyzed for triple bonds and by dehydrogenating a part of the catalyst on Adams platinum, the total content of unsaturated bonds was determined. One of the resulting graphs is sketched in Figure 2.

Hexine-1 almost instantaneously extracts a part of the adsorbed hydrogen from the catalyst (54 ml from 1 g Ni). There then follow the sequential-parallel processes of simultaneous hydrogenation of the alkene and the alkane and the saturation of the catalyst with hydrogen from the gaseous phase. On small quantities of the catalyst, there first takes place the selective hydrogenation of hexine-1 to hexene-1. The formation of a saturated product begins on reaching that concentration of the olefin which is maximal under the experimental conditions and is accompanied by a sharp break on the kinetic and the potential curves. In all cases the concentration of the n-hexane increases, according to an equation of the first order.

It is known from the work of Elovich, Zhabrova and Goldansky [9-11] that the effect of the amount of catalyst on the rate of reaction is determined by the limiting step of the process. With an increase in the amount of catalyst, there is a rise in the intensity of the consumption of the reaction components, a transition from the kinetic to the diffusional, or even into the "solution" region being observed.

It should, however, be taken into account that the kinetics of hydrogenation on a Raney nickel catalyst is determined by three mutually interacting processes: the hydrogenation of the material at the expense of hydrogen from the gaseous phase, and the dehydrogenation and subsequent saturation of the catalyst [12, 13]. The effect of each of these processes on the integral rate of reaction depends on the size of the charge of catalyst. As has been shown in [14], the extraction of 70% of the hydrogen from a Raney nickel catalyst diminishes the surface of the latter by only 10-12%, whereas further dehydrogenation leads to a sharp contraction in this active surface. These peculiarities of the hydrogenation on Raney nickel are the cause of the above-noted dependence of the magnitude of the energy of activation on the amount of catalyst. In this case, the energy of activation refers to the sum of the processes of hydrogenation, dehydrogenation and saturation, and with small Ni charges is approximately equal to the value characteristic for compounds with a triple bond [12].

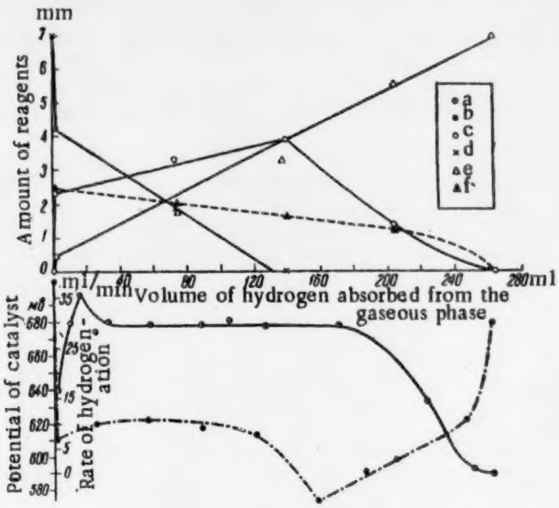

Fig. 2. The hydrogenation of hexine-1 on a Raney nickel catalyst. Amount of catalyst, 1.128 g; hexine-1, 0.5728 g; temperature, 20°; intensity of agitation, 250 vib/min; solvent, absolute alcohol. a) Kinetic curve; b) potential curve; c) amount of hexene-1 in the products of catalysis; d) amount of hexine-1 in the products of catalysis; e) amount of n-hexane in the products of catalysis; f) amount of hydrogen extracted from the catalyst.

Substances with triple and conjugate bonds are firmly absorbed on contact with metals and are activated during hydrogenation on the same centers as hydrogen. Thus, the rate of reaction is limited by the activation of the hydrogen when the amount of catalyst is small and by the transport of reacting molecules, predominantly hydrogen, to the catalyst surface when this amount is large. The transition from one limiting mechanism to the other results from altering the ratio between the amount of the catalyst and the amount of the compound which is being hydrogenated and also from varying the intensity of agitation, the temperature, the volume and form of the reaction vessel, etc. Thus, measurement of the catalyst potential permits the establishment of the effect of various factors on the mechanism of the hydrogenation reaction and can be successfully applied for searching out the optimal ratio between the amounts of catalyst and reacting substance.

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THE RELATION BETWEEN THE STRUCTURE OF A MAGNESIUM ALLOY AND ITS TENDENCY TO CORRODE UNDER STRAIN

M.A. Timonova

(Presented by Academician A.A. Bochvar, June 6, 1957)

Among the known magnesium alloys, the high elastic alloys of the Mg–Al–Zn–Mn system show a marked tendency toward corrosion under strain. Up to the present time, the mechanism of the corrosional disintegration of these high elastic magnesium alloys has not been developed and for this reason the continuing search for radical methods of treating them so as to prevent corrosional disintegration have not met with success [1-4].

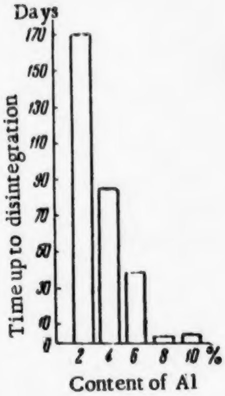

Fig. 1. The influence of aluminum on the tendency of alloys from the Mg–Al system to corrode under strain.

Our work on the mechanism of corrosional disintegration has established the following points:

1. Aluminum is the principal alloying component which is responsible for the tendency toward corrosional disintegration in the magnesium alloys of the Mg–Al–Zn–Mn system, this tendency to corrosion in the atmosphere appearing only at such aluminum concentrations as lead to the formation of supersaturated solid solutions, i.e., at concentrations of aluminum in excess of 2-3%. Alloy strength is increased by increasing the percentage of aluminum but the resistance to corrosion under strain is diminished.

In Figure 1 there is shown the influence of aluminum on the corrosional disintegration of binary Mg–Al alloys.

2. The corrosional disintegration of magnesium alloys results from the selective dissolution of the supersaturated solid solution, or of the intermetallic compound Mg_4Al_3, and the resulting formation of microfissures.

Starting from these ideas, we have come to the conclusion that an alloy will fail to disintegrate only in the event that it does not contain continuous chains of deposits of the intermetallic compound Mg_4Al_3, or the supersaturated solid solution, to serve as zones for the disintegration.

A magnesium alloy which is not inclined to corrosional disintegration must have a structure showing an aluminum-lean solid solution and uniformly distributed, separate particles of the intermetallic compound.

We have made the attempt to obtain magnesium alloys of this structure by selecting such a method of thermal treatment as would lead to complete breakdown within the grains. This complete breakdown within the grains is achieved during long heating in the temperature interval 175-250° [5]. At lower temperatures, the breakdown of the supersaturated solution proceeds very slowly. For ease of investigation a pressed binary Mg + 8% Al alloy was chosen for study.

From the phase diagram it follows that the solid solution contains 2.9% aluminum at 175°, 3% at 185°, and 3.8% at 250°.

To obtain the requisite disintegration, we carried out an extensive thermal treatment of the alloy over 5 days at a temperature of 185°. In order to further deplete the solid solution of aluminum, i.e., in order to bring its aluminum content down to 2%, an additional treatment was carried out at lower temperatures, 60-100°, in the course of 15-30 days.

Specimens of the alloy were subjected to various programs of thermal treatment. After thermal treatment, the surfaces of the specimens were cleaned with sandpaper and washed with ethyl alcohol. Various sections of the test specimens were compared [6].

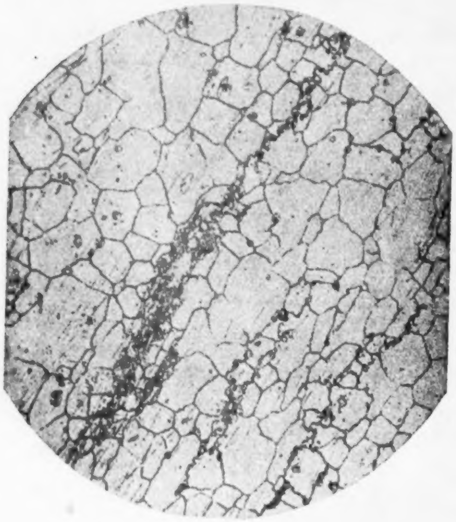

Fig. 2. The microstructure of a Mg + 8% Al alloy in the hot-pressed condition. x 200.

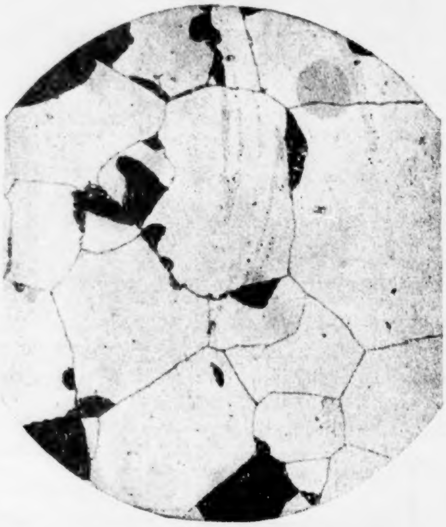

Fig. 3. The microstructure of a Mg + 8% Al alloy in the tempered condition (tempered in air from a temperature of 420° over 24 hours) with subsequent aging for 10 hours at 175°. x 200.

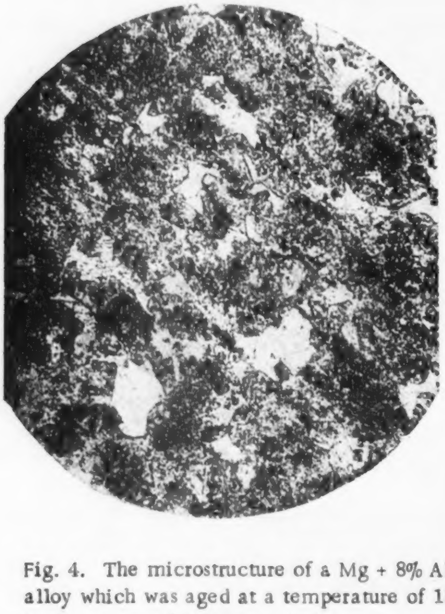

Fig. 4. The microstructure of a Mg + 8% Al alloy which was aged at a temperature of 185° in the course of 5 days. x 200.

Tension was applied on a Shoper machine, starting at a value equal to 90% of the quantity $\sigma_{0.2}$. Calculation of the tension was carried out according to the equation $P = \sigma bh/6x$, in which P is the force required for obtaining the desired tension; σ is this tension; $\underline{b}$ is the width of the specimen at the position of the section; $\underline{h}$ is the specimen thickness, and $\underline{x}$ is the distance from the point of application of the force to the section. The corrosional experiments were carried out under variable loading of the specimens in 0.001% NaCl solution. The time required for the appearance of the first fissuring was determined.

In Figures 2, 3 and 4 there are shown microstructures of the alloy after various types of thermal treatment. From a study of these microstructures it can be noted that in the hot-pressed condition (Figure 2), the alloy consists of a supersaturated solid solution of aluminum in magnesium and the intermetallic compound Mg_4Al_3, the latter being distributed along the grain boundaries (boundary thickening). In the tempered (homogenized) condition, the alloy is a "microscopically" uniform, supersaturated solid solution. The large grain growth is to be noted, this obviously resulting from recrystallization during the tempering process.

During a brief aging of the tempered alloy, there occurs a partial breakdown of the supersaturated solid solution, principally at the grain boundaries (Figure 3). Without preliminary homogenization, breakdown is not observed during extended heating over 30 days at a temperature of 80°. Breakdown within the grain results from aging over 5 days at a temperature of 185° (Figure 4).

It should be pointed out that after heating during 5 days at a temperature of 185°, no visible changes result from an additional treatment over 15-30 days at 60-100°.

Thus, it is clear that there is an essentially complete breakdown of the supersaturated solution during extended treatment at a temperature of 185°. After such treatment, the alloy must consist of a solid solution containing 3% Al, which is not subject to corrosional disintegration under the given conditions, and of individual, disconnected particles of the intermetallic compounds. The result of corrosional experiments proved to be as follows:

No. of thermal treatment	1	2	3				6		7		8		9		10		11	
Temperature of heating, °C	Without thermal treatment (hot pressed)	420	420	175	80	185	185	60	185	60	185	80	185	80	185	100	180	100
Duration of heating, days		1	1	0.4	30	5	5	15	5	30	5	15	5	30	5	15	5	30
Time to fissuring of specimen, days (mean for 5 specimens)	18	10	15			50	Not subjected to fissuring in the course of 1 year											

A study of the data obtained indicate that in the hot-pressed, tempered, aged condition (incomplete breakdown), an alloy under strain will show corrosion after a comparatively short period of time. Extended heating at 80° does not lead to a microscopically detectable breakdown and does not prevent corrosional disintegration.

Long heating at 185° leads to breakdown within the grains and to the separation of the intermetallic compound in the form of individual particles and prevents corrosional disintegration. Such specimens were not subject to corrosional disintegration over a period of 360 days. These experiments were broken off because of extensive general corrosion of the specimens. It should also be pointed out that the thermal treatment which was applied at 185° did not impair the mechanical properties of the alloy. For the solution of the practical problem connected with the elimination of the tendency of magnesium alloys to corrosional disintegration, it is indispensable to establish the minimum time of heating which would guarantee a complete breakdown of the solid solution at a given temperature. It is very likely that the duration of this heating would be considerably less than the 5 days which has been established in our experiments.

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THE INFLUENCES OF SOME FEATURES OF MOLECULAR INTERACTION ON THE REGULARITIES OBSERVED IN DEUTERON EXCHANGE

A.I. Shatenshtein and E.N. Zvyagintseva

(Presented by Academician A.N. Terenin, May 24, 1957)

The rules governing deuteron exchange in a substance depend on the details of its interaction with the solvent. Usually isotopic exchange of the hydrogen in hydrocarbons proceeds more rapidly with protophilic and protogenic solvents than with amphoteric, and the more rapidly,the stronger the protolytic (acidic or basic) nature of the hydrocarbon [1]. On turning to a consideration of the exchange of the hydrogen of the C–H bonds of organic compounds containing nitrogen, it can be shown that the process proceeds in a different fashion. Thus, the ortho-para hydrogen atoms of an aromatic amine exchange the more rapidly with liquid DBr, the weaker the basic properties of the amine, this being due to the fact that by the energetic interaction of the amine and the acid, a deuteron is combined with the free pair of electrons of the nitrogen atom to form a positively charged ion with tetravalent nitrogen and the conjugation between the p-electrons of nitrogen and the π-electrons of the aromatic ring is thereby destroyed, this in turn, impeding the binding of deuterons to the carbon atoms of the ring and the exchange with the hydrogen atoms which are bound to them [2]. In addition, the formation of a positive charge can result in an electrostatic repulsion of the deuterons in solvents such as liquid DBr ($Dn_{-80} = 6$) which have a low dielectric constant. It will be shown below that the enhanced rate of hydrogen exchange of quinaldine and α-picoline with alcohol as compared with the protophilic liquid ammonia can be explained in terms of the change in the valence state of the nitrogen atom in the methylated heterocycle which results from the formation of complexes with this amphoteric solvent.

At the present, a direct comparison of the rates of deuteron exchange with alcohols and with liquid ammonia is not to be found in the literature. For such comparison we have, in the present work, carried out experiments not only with the nitrogen heterocycles which have been mentioned above, but with hydrocarbons (indene and fluorene) and with ketones (acetophenone and β-naphthylmethylketone) as well. It was, first of all, shown that the same atoms of hydrogen are exchanged with both solvents; these are the atoms of the CH_2-groups in indene and fluorene, and the atoms of the CH_3-groups in the other substances. Deuterium,which has been introduced into a substance by exchange with C_2H_5OD, is washed out by subsequent treatment with liquid ammonia (reverse exchange). It was incidentally established that 3 atoms of H in the molecule of indene exchange with ND_3 and with solutions of $C_2H_5O^-$ in C_3H_5OD, whereas with a solution of DCl in C_2H_5OD at 150° there is an exchange of a single H atom which is not one of those participating in the reaction with the bases. With a solution of DCl in C_2H_5OD at 180° there takes place a slow partial exchange of the hydrogen in the aromatic portion of the fluorene molecule.

From the values of the velocity constants (sec^{-1}),which are presented in Table 1, it is to be seen that the exchange of the hydrogen of the hydrocarbons and the ketones with liquid ammonia proceeds at considerably lower temperatures and higher velocities than does the exchange with ethanol. One H atom of fluorene, for example, exchanges with liquid ammonia in 1 hour at 25°, and with ethanol in 2000 hours at 180°. Using the approximate values of the energy of activation for exchange of the H in acetophenone and in fluorene (12 and 11 kcal), we have become convinced that the most mobile H atoms in these materials exchange by 4 and 6 orders more rapidly with liquid ND_3 than with C_2H_5OD. On the other hand, the hydrogen of the methyl groups of the nitrogen heterocycles exchanges by one order more slowly with ammonia than with ethanol. These experiments were carried out at 120° using three specimens of quinaldine (I, II, III) and two of α-picoline. Quinaldine with ammonia ($k \cdot 10^7$ sec^{-1}) I: 1.0; 0.7; II: 1.0; 0.8. Picoline with ethanol ($k \cdot 10^8$ sec^{-1}): 3, 2. For example, with a concentration 25 mole % of D in the solvent and after 230 hours, the concentration of D in the water resulting from combustion of the quinaldine amounted to 3.5 at.% in experiments with C_2H_5OD, to 0.6 at.% in experiments with ND_3 and to 0.2 at.% in experiments with alcoholic solutions of picoline, the H of the picoline failing to exchange with ND_3 in this period.

Experiments on the reverse exchange were performed with quinaldine which had been previously deuterized. By measuring the physical constants it was shown that these substances did not change during the time of experiment. Purification was carried out prior to isotopic analysis. Careful control confirmed the fact that the separation and purification of the materials following experiment (for example, by precipitation in the form of picrates, by decomposition, etc.) did not change the isotopic composition.*

TABLE 1

Substance	C_2H_5OD	ND_3	$C_2H_5O^- + C_2H_5OD$
Indene	10^{-6}—10^{-7} (150°)	$1 \cdot 10^{-4}$ (—10°)	0.05 *N* $3 \cdot 10^{-5}$ (0°)
"	—	$4 \cdot 10^{-4}$ (0°)	1 *N* $7 \cdot 10^{-4}$ (0°)
"	—	$9 \cdot 10^{-4}$ (10°)	—
Fluorene	$1 \cdot 10^{-7}$ (180°)	$2 \cdot 10^{-4}$ (25°)	1 *N* $6 \cdot 10^{-4}$ (25°)
Acetophenone	$2 \cdot 10^{-7}$ (120°)	$1.1 \cdot 10^{-5}$ (0°)	1 *N* $4 \cdot 10^{-5}$ (0°)
"	—	$6.5 \cdot 10^{-5}$ (25°)	—
"	—	$1.3 \cdot 10^{-4}$ (40°)	—
β-Naphthylmethylketone	10^{-6}—10^{-7} (120°)	$1.5 \cdot 10^{-5}$ (0°)	—
Quinaldine	$2 \cdot 10^{-6}$ (120°)	$8 \cdot 10^{-8}$ (120°)	0.1 *N* $1 \cdot 10^{-4}$ (120°)
Picoline	$3 \cdot 10^{-8}$ (120°)	—	0.1 *N* $1 \cdot 10^{-6}$ (120°)
"	—	—	1 *N* $3 \cdot 10^{-5}$ (120°)

Note: The velocity constants for the exchange of the first four materials with alcohol are tentative values. The experiments with indene in alcohol were distinguished by poor reproducibility, which possibly resulted from a partial polymerization of this material. The three specimens of indene gave identical values for the velocity constant for the exchange with liquid ammonia. The velocity constants for the exchange of indene, fluorene and acetophenone with ND_3 were determined with greater precision than was the case in [3].

In order to understand the nonuniform behavior of various groups of compounds in the reaction of H exchange, it is necessary to become familiar with acid-base properties of these substances. The compounds which are enumerated below behave as weak acids when dissolved in liquid ammonia and are converted to carbanions on addition of bases. Judging from the velocity constants for the exchange of their hydrogen with liquid ND_3 (at 120°, or recalculated to this temperature), their relative acid strengths diminish in the sequence: indene ($4 \cdot 10^1$) > fluorene ($2 \cdot 10^{-2}$) > acetophenone ($4 \cdot 10^{-3}$) > triphenylmethane ($2 \cdot 10^{-7}$) > quinaldine ($7 \cdot 10^{-7}$) > diphenylmethane ($7 \cdot 10^{-9}$) > α-picoline ($< 10^{-8}$).**

Indene and fluorene are extremely weak acids in alcoholic solutions and acetophenone a very weak base; the dissociation constants of quinaldine and picoline are of the order of 10^{-9}. Measurements of the infra-red spectra [6, 7] have shown that hydrogen bonding arises between the hydrogen of the OH groups of the alcohol and the nitrogen of the heterocycle, as a result of which the valence state of the N atom is altered in a certain degree, acquiring the character of N^+ and facilitating the protonization of the H atoms of the CH_3-groups. It is well known that the mobility of the hydrogen of CH_3-groups is sharply increased by the formation of the alkylate halides of quinaldine and picoline due to the ionization of the nitrogen [8]. Thus, by reacting with the alcohol as a base, molecular compounds of quinaldine and picoline are formed whose acidity markedly exceeds that of the initial substances.

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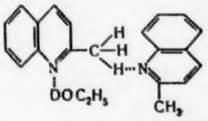
*It was observed in passing that if solid alkali is present in an ammoniacal solution of quinaldine there occurs a very rapid isotopic exchange of the hydrogen of themethyl group, this being tied up with the formation of the potassium salt of quinaldine. Thus KOH in NH_3 metallates organic compounds (see [4]). Measurements of the adsorption spectra of ammoniacal solutions which have been carried out by I.V. Astafyev have shown that it is possible, in this manner, to obtain carbanions of indene, fluorene, tri- and diphenylmethane, as well as anions of the aromatic amines. The superiority of KOH, in comparison with KNH_2 [2], is found in the fact that it becomes possible to measure the absorption spectra of the ammoniacal solutions of the carbanions in the ultraviolet region.

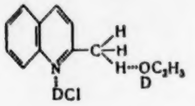
**These constants are expressed in sec^{-1}. The data for fluorene were obtained by Yu.P. Vyrsky and E.A. Yakovleva and those for tri- and diphenylmethane by E.A. Yakovleva.

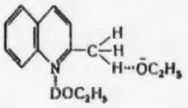
Judging from the measurement of Hine and Hine [9], the acidity of the alcohols increases in the order: iso-propanol (I) < ethanol (II) methanol (III) < ethylene glycol (IV).* Our experiments, which were carried out with carefully dehydrated alcohols, have shown that the velocity constants for exchange with the hydrogen in quinaldine increase in the same sense (120°). I. Isopropanol ($k \cdot 10^7$): 9, 9, 10, 5 (direct exchange); 11, 7, 4, 9 (reverse exchange). II. Ethanol ($k = 2 \cdot 10^{-6}$) (see Table 1). III. Methanol ($k \cdot 10^6$): 3.0, 3.0 (direct exchange); 2.6, 2.9, 2.3 (reverse exchange). IV. Ethyleneglycol ($k \cdot 10^6$): 9.2, 9.2, 9.1, 9.1 (reverse exchange). For example, in certain experiments with these alcohols (120°, 105 hours), the concentration of deuterium in the water from the combustion of the quinaldine was: I, 4.9; II, 2.2; III, 2.0; IV, 0.2 at.% (prior to experiment, 6.3 at.% D).

Taking into account what has been said, it can be supposed that the rate of the exchange reaction is increased by raising the polarity and the concentration of the heterocycle complexes. Actually, the addition of hydrogen chloride to an ethanol solution of quinaldine in an amount equal to 0.2 moles/mole of base increases the rate of the exchange reaction by two orders ($k_{120°} = 5 \cdot 10^{-5}$ sec^{-1}). With a ratio of 0.5 moles/mole of base, $k_{120°} = 7 \cdot 10^{-5}$ sec^{-1}, but with an equal molar ratio of acid and quinaldine, $k_{120°} = 4 \cdot 10^{-6}$ sec^{-1} (see [10]). (Control experiments have established that DCl reacts with alcohol to form C_2H_5Cl only if it is present in excess of stoichiometric portions.) A more rapid deuterium exchange must be expected with the alkylate halides of quinaldine as compared with the quinaldine itself.

In order that an exchange reaction take place, the proton of the CH_3-group must be transferred to some base. As long as the solution contains an excess of the nitrogen heterocycle which is unneutralized by the acid, the molecules of the former (some of which may be unsolvated) fulfill the function of proton acceptors. On complete neutralization of the base by the acid, the rate of the exchange action diminishes because the molecules of the solvent, a base weaker than quinaldine, then become the proton acceptors. If, on the other hand, an alcoholate, a base stronger than quinaldine, is added to an alcoholic quinaldine solution, the reaction rate sharply increases (recalculated to a 1 N alcoholate solution, $k_{120°} \simeq 10^{-3}$). Thus, complexes of various compositions participate in the reaction in neutral, acidic and alkaline solutions**:







It is clear that the complex of quinaldine with alcohol does not break down in the presence of the alcoholate. The rate of exchange of the hydrogen of quinaldine with a 1 N solution of alcoholate in ethanol is at least four orders higher than the rate of exchange with liquid ammonia, whereas with indene, fluorene and acetophenone the corresponding rates differ only by several fold (see Table 1).

The presence of potassium amide in ammoniacal solution (0.2 moles/mole of quinaldine) results, even at −31°, in an exchange with a rate of $2 \cdot 10^{-5}$ sec^{-1}, i.e., the exchange is more rapid by three orders than at 120° without a catalyst. We note that the potassium amide is neutralized by the quinaldine, the latter being converted into the potassium salt, and the concentration of the NH_2^--ions is accordingly very low.

There is a definite analogy between the acid catalysis of the deuteron exchange in alcoholic solutions of quinaldine and the alkali catalysis of the exchange of the hydrogen of the aromatic phenol ring with heavy water [11]. In the work of Ingold, as in our own, the reactivity of the substance in which the exchange reaction was taking place was increased as a result of the acid-base interaction with a protolyte introduced from the outside. The excess of the unreacted material participated in the exchange reaction, fulfilling the inverse protolytic function with regard to the catalyst.

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*In this same sequence, the dielectric constants increase as: 15.7, 25.7, 33.0, 37.7. The dipole moment of ethylene glycol is equal to 2.28 D; the values for the remaining alcohols are identical (1.77-1.8 D).

**It is natural that the solvent, which is a deuteron donor, should participate in the reversibly reactive complexes.

It should also be noted that there is an analogy between the here-described nonuniformity in the relative rates of the exchange of the hydrogen of hydrocarbons, ketones, and methylated heterocycles with alcohol under catalysis by $C_2H_5O^-$ and with liquid ammonia and the reported alteration in the relationship of the ionization constants of acids of various classes which arises on transition from one solvent to another, this latter being explained by the formation of products of different structures as the result of interaction of the acids and the solvents [12].

All of the facts which have been outlined show that the principles of deuteron exchange strongly depend on the peculiarities of the molecular interaction in solution.

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* Original Russian pagination. See C.B. Translation.

THE EFFECT OF SUBSTITUENTS ON THE PROPERTIES OF THE MOLECULES OF MONODERIVATIVES OF BENZENE

P.P. Shorygin and Z.S. Egorova

(Presented by Academician V.N. Kondratyev, July 6, 1957)

The monoderivatives of benzene form one of the most important groups of organic compounds. In a considerable degree their chemical and physical properties are determined by the mutual interaction of the substituent and the benzene ring. This is reflected in the heats of formation, the interatomic distances, the vibrational frequencies, the ultraviolet absorption spectra, the magnetic susceptibilities, the probabilities of transitions in the infra-red and the Raman spectra, the dipole moments, and in other properties as well.

In this work there have been investigated certain monoderivatives of benzene, PhX, which contain alkyl groups, halide atoms and other groups of various types as the substituent X.

We have turned our attention principally to the question as to whether there is any similarity in the various measures of the influence of a substituent on the benzene ring. One such measure is the increase in the intensities of the characteristic lines of the benzene ring (1000 ± 10 cm^{-1} and 1600 ± 20 cm^{-1}) in the Raman spectra. In benzene and in the benzene alkyls, the line at ~ 1600 cm^{-1} is of low intensity; its intensity is considerably greater in derivatives containing substituents which are capable of more or less strongly interacting with the benzene ring. The intensity of the line at 1600 cm^{-1} can serve as a basis for making certain preliminary estimates of the polarizability of that part of the molecule which depends on the nuclear coordinates of the benzene ring.

In Table 1 there have been compiled: 1) the results of measurements of the coefficient of integral intensity of the 1600 cm^{-1} line of the benzene ring in the Raman spectra (I_{1600}); 2) values of the exaltation of the molecular refraction, for $\lambda = 5893$ A (EMR_D) and for $\lambda = 4361$ A (EMR_γ)*; 3) the positions of the intense adsorption bands (the wavelengths of the λ maxima, in A), values of $\epsilon/1000$, where ϵ is the molar (decimal) coefficient of absorption at the band maximum, being given in parentheses**; 4) the anomaly in the dipole moments ($\Delta\mu$, the difference between the μ vectors for the compounds PhX and AlkX (Alk = Me, Et) in debyes, according to the data on μ in benzene); 5) the Hammet constant, σ_n, which determines the influence of a substituent on the reactivity of groups located in the para position. In this table mean values from the literature have been used for μ, MR, σ, and λ; the data on the absorption spectra which are shown with the mark * are from our measurements.

The intensity coefficients of the lines of the Raman spectra were measured in CCl_4 solutions, using a photographic method; dimethyl aniline and nitrostyrol were studied in cyclohexane. A number of these coefficients were also determined by the photoelectric method of V.P. Bazov. In the case of divergencies, mean values were selected. As a unit there was selected 1/100 of the integral intensity of the 313 cm^{-1} CCl_4 line, calculated to 1 mole. The accuracy mounted to ±10%. The spectra were excited by the 4358 A line of mercury. The data for phenylbutadiene were obtained by B.M. Medvedeva, those for aniline by Z. Alaune and those for ethyl acetanalide by T.N. Shkurina; the figures accompanied by the sign ($^+$) are according to the results of [1]. For

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*EMR values were obtained by comparing the refractions of PhX and AlkX; here the exaltation which is already present in the AlkX (for example, in Alk. $CH:CH \cdot NO_2$), does not come into play.

**We neglect the presence of a fine structure in the first band.

TABLE 1

Group X in PhX	I_{1600}	EMR_D	EMR_γ	Ultraviolet absorption spectra (in heptane)			Δu	σ_n
				λ_1	λ_2	λ_3		
·C : C·NO_2	3500	4.0	—	—	3000 (17)	22[illegible]0 (10)	—	—
·C : C·Ph	3000⁺	5.0	—	—	2950 (25)	2250 (15)	~0	0.3
·C : C·CHO	2000	3.3	5.1	—	*2790 (25)	2200 (13)	—0.2	—
·C : C·COOEt	1400	3.1	4.6	—	*2720 (21)	2160 (17)	—	—
·C : C·C : C	1100	3.0	—	—	2800 (25)	2230 (12)	~0	—
·Ph	360⁺	2.0	—	—	2470 (18)	2070 (27)	~0	0
·C : C	240⁺	1.4	2.0	2820 (0.8)	2450 (13)	2030 (22)	—0.1	0
·NO_2	210	0.9	1.4	2800 (1.5)	2520 (9,6)	—	—0.9	1.0
·CHO	200⁺	1.1	1.45	*2800 (1.5)	2420 (14)	—	—0.55	0.8
·NHCHO	190	—	—	*2750 (1)	2400 (13)	—	—	0
·COR	180⁺	0.85	1.15	2800 (1)	2380 (13)	—	—0.5	0.7
NR_2	160	1.6	2.3	2970 (2)	2500 (14)	2000 (22) 1760 (36)	1.5	—0.6
·CN	140⁺	1.0	1.2	2740 (0.6)	2250 (12)	—	—0.4	0.8
·COOR	120⁺	0.75	0.95	2770 (0.9)	2290 (12)	—	—0.2	0.6
·NHR	110	1.25	1.75	2880 (1.8)	2380 (14)	2000 (21)	—	—0.6
·SR	110	0.80	1.10	2790 (1.5)	2550 (10)	2050 (12)	0.5	0
·SH	100	0.50	0.70	2690 (0.7)	2360 (9)	—	0.5	—
·NH_2	85	0.95	1.30	2850 (1.7)	2330 (8)	2000 (20)	0.9	—0.5
·NEt·COR	80	—	—	—	*2380 (5.5)	—	—	—
·CCl_3	80	0.35	—	*2680 (0.6)	2240 (7)	—	—0.55	0.45
·OR	50⁺	0.35	0.50	2720 (1.8)	2200 (8)	—	0.9	—0.2
·OH	40	0.28	0.37	*2700 (1.8)	2130 (6)	—	0.7	—0.25
·I	42	0.15	0.20	2570 (0.7)	2310 (12)	—	0.2	0.3
·C·C·Ph	45	—	—	2600 (0.5)	~2050 (19)	1870 (100)	—	—
·R	39	0.27	0.31	2620 (0.3)	2050 (8.1)	1870 (55)	0.35	—0.15
·CR_3	32	0.20	0.24	2600 (0.3)	2060 (9)	1880 (80)	0.5	—0.2
·SO_2R	(~30)	—	—	*2700 (1)	2160 (8)	—	—0.4	0.8
·Br	33	0.10	0.15	*2650 (0.3)	2150 (9)	—	0.2	0.2
·Cl	33	0 15	0.17	*2650 (0.3)	2150 (8)	—	0.2	0.2
·F	~28	—0.05	—0.15	2670 (1.2)	2010 (7 3)	1810 (50)	0.2	0
·D	35	0	0	—	—	—	0	0
·H	35	0	0	2550 (0.2)	2020 (7.3)	1820 (50)	0	0

Note: H atoms which are attached to carbons have been omitted from the formulas; R is the methyl group.

dibenzyl, stilbene, and diphenyl, the values given are for $0.5 \cdot I_{1600}$.*

In the region of 1600 cm^{-1}, benzene, toluol, fluorobenzene and phenol each have two lines; the values given in the table are for the total intensity of both lines. It is clear that there are two modes of vibration of the benzene ring in PhX; these vibrations differ slightly from one another in frequency and one of them is symmetrical (in the case of a pronounced influence from the substituent, the ~1600 line is rather strongly polarized [2]).

It is to be seen that alkyl groups have but little effect on the optical, chemical and electrical properties of PhX. Substituents containing double bonds, C=C, and benzene rings strongly affect the optical properties and have little influence on the chemical characteristics and the dipole moments. Strongly electropositive and electronegative substituents markedly influence all of these properties.

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*For certain compounds which have been studied earlier the intensity coefficients given in Table 1 differ from the old values and are more exact (see the data on dibenzyl). According to the measurements in cyclohexane, the value $0.5\ I/_{1600}$ for dibenzyl is about 70, i.e., it is larger than in CCl_4. With toluol, identical values of I_{1600} were obtained in both solvents.

A certain similarity is observed between the various measures of the influence of the substituents on the optical properties; in most cases, the closer and the more intensive the absorption bands, the higher is the intensity of the 1600 line and the EMR. At the same time there is an undoubted relation between the anomaly in the dipole moment and the constant σ; the electronegative substituents have, in most cases, positive values of σ_n and the electropositive, negative values (roughly speaking, the larger $\Delta\mu$, the smaller σ_n*). These optical properties, however, do not clearly conform with the electrical and chemical characteristics.

From the positions and intensities of the absorption bands there can be calculated the contribution, R_i, which each of the various electron levels makes to the molecular refraction, MR, use being made of the equation $R_i = 18 \cdot 10^9 \cdot f_i (\nu_i^2 - \nu^2)^{-1}$, in which ν_i is the frequency of the i-th absorption band, ν the frequency of the incident light in cm^{-1} and f_i the strength of the oscillator.

TABLE 2

Compound	Absorption bands (λ in mμ)									ΣR	$MR_\gamma - MR_D$	
	1st			2nd			3rd and 4th					
	λ_1	R_1	ΔR_1	λ_2	R_2	ΔR_2	λ_3	R_3	ΔR_3		calc. $\Sigma\Delta R$	Exp.
Benzene	255	0.06	0.01	204	1.3	0.16	184	7.3	0.70	8.7	0.87	0.96
Fluorobenzene	267	0.4	0.11	200	1.2	0.15	181	7.0	0.67	8.6	0.93	0.87
Toluol	262	0.1	0.02	205	1.6	0.20	189	7.9	0.78	9.6	1.00	1.10
Tertiarybutylbenzene	260	0.1	0.02	206	1.6	0.22	188	11.9	1.26	13.6	1.50	1.36
Styrol	282	0.3	0.11	245	3.6	0.73	203	4.0	0.50	7.9	1.33	1.80
Dimethylaniline	297	0.9	0.37	250	3.8	0.82	200	3.9	0.46	—	—	—
							176	4.7	0.43	13.3	2.08	2.06
Cinnamic aldehyde	—	—	—	279	10.1	3.20	220	3.0	0.48	13.1	3.68	3.55

In Table 2 there are given values of R_i, expressed in cubic centimeters, which have been calculated for the sodium D line and increments (ΔR_i) of these values for conversion from the D line to the H_γ line of hydrogen (4361 A).

It is to be seen that for some of these compounds ΣR_i considerably exceeds the value of ΣR_i for benzene, the difference here being much larger than the EMR values found experimentally. Supposing the working equation and the experimental data for ϵ to be correct, the indication is that the study of the first three absorption bands is definitely inadequate for the elucidation of the exaltation, additional bands being able to effect a diminution in EMR (i.e., they are weaker and further displaced than in benzene). There is no doubt that it is impossible to ascribe the exaltation to a single absorption band.

Because of the peculiarities of resonating substituents, the proximity of the absorption bands must be of greater significance for the dispersion and intensity of the lines in the Raman spectra than for refraction. In the same way, bands in the region > 1700 A can, in principle, explain the observed values of $MR_\gamma - MR_D$; in actuality, the latter do not markedly differ from the calculated values of $\Sigma\Delta R$ (see Table 2).

Judging from the available data on the relation between the values of I_{1600} for styrol and for benzonitrile and the frequency of the incident light, ν, the electron levels which are of greatest significance for I_{1600}, are those lying in the region 1700-2500 A.

The observed similarities in the variations of EMR and I_{1600} may be interpreted as indicating that some, at least, of the various parameters on which these quantities depend are held in common; such parameters could be the ν_i and f_i values of the intense absorption bands.

There is no justification for relating the exaltation of the PhX refraction to the atoms of the substituent X (Ingold [3]) or to the C_{ar}–X bonds [4]. Relating it to the benzene ring would be more nearly justified, although even this is rather arbitrary. The intensity of the 1600 cm^{-1} line is, in all likelihood, tied up to a considerable degree with the benzene ring. It must be kept in view that the intense absorption bands in the region 1800-3000 A are largely due to the benzene ring or to the "benzene ring-substituents" system.

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* The concordance is, however, very approximate. Here there should be kept in view not only the specific nature of the chemical processes (the significance of which can in part be judged from the fact that for various reactions the constants σ alter over wide limits) but also differences in the solvents.

Table 1 indicates that no general parallelism is to be observed between the various effects of the mutual interaction of the atomic groups in the PhX molecules. In this connection, it should be noted that the concepts of "stronger" and "weaker" interaction of atomic groups can be employed only in a very narrow and arbitrary sense in dealing with a definite effect of approximately uniform character in a series of similar compounds.

In the various optical properties a greater concordance is observed between the manifestations of the mutual interaction of groups. For more precise comparisons, more complete information is needed on all the levels of electronic excitation.

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SIGNIFICANCE OF CHAIN REACTIONS IN THE HIGH TEMPERATURE CRACKING OF ETHANE

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The part played by chain reactions in the cracking of ethane in the temperature interval 770-900° is discussed in this paper. This problem has been intensively studied for lower temperatures in recent years [1-3, 8]. However, the mechanism of the cracking and pyrolysis reactions, especially at the high temperatures used in industry [4], cannot be considered to have been fully elucidated.

To solve the problem in question, we measured the activities of the various products, obtained in the cracking of a mixture of ethane and methane, the latter labeled with radioactive carbon C^{14}. The indicated experiments were run by the procedure described in paper [5]. The data, obtained for the three temperatures: 770, 840 and 890°, are presented in Table 1. In treating the results it was assumed that the discussed experiments were run under conditions of complete or nearly complete mixing in a "boiling" layer [5]. This permits reducing the problem to one of solving a system of algebraic equations.

TABLE 1

t, sec.	Temperature, °C	$\frac{\text{Activity of obtained gases}}{\text{Activity of original mixture}} \cdot 10^6$ *				
		C_2H_6	C_2H_4	C_3	C_4	CO_2 (coke)
0.14	770 ± 3	7.1 ± 3.3	5.4 ± 1.5	15.8	0.14	2.8 ± 0.1
0.185		8.6 ± 3.7	7.9 ± 1.9	38	0.65	—
0.260		14.4 ± 5.6	13.8 ± 2.8	42.5	1.64	3.94 ± 0.2
0.415		19 ± 4.7	22 ± 1.9	74	3.5	6.35 ± 0.4
0.82		24 ± 5.6	52 ± 3.7	131	10.3	17.2 ± 0.9
0.008	840 ± 3	10.8 ± 5	9.32 ± 0.5	—	—	5.05 ± 0.1
0.026		80.5 ± 5	67.2 ± 2	—	—	14.4 ± 0.6
0.0415		80.5 ± 3	93.5 ± 5	—	—	28.8 ± 0.3
0.0625		86 ± 4	107 ± 3	—	—	30.7 ± 1.5
0.0735		75 ± 4	135 ± 5	—	—	—
0.0078	890 ± 3	87	146.5	248	9.75	0.35
0.0117		99	162	271	13.9	4.25
0.0152		126	247	400	24.2	17.3
0.0156		124	254	402	24	14.2
0.0192		138	297	477	39.5	—

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* In those cases where the error in measuring activity is not indicated, it does not exceed 3%.

Retaining the designations adopted in [5], we will additionally introduce the following elementary processes in the discussion.*

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* The influence of possible participation in the reaction of an additional molecule M can be included in the corresponding constant, since the experiments were run at a constant pressure.

$$C_2H_6 \rightarrow 2CH_3; \tag{1}$$

$$CH_4 \rightarrow H + CH_3; \tag{1'}$$

$$R_i + R'H \rightarrow R_iH + R'; \tag{2}$$

$$R_i + R_j \rightarrow R_iR_j; \tag{3}$$

$$C_2H_5 \rightarrow C_2H_4 + H \tag{4}$$

with the constants respectively equal to k_1, k'_1, $k_{2(R_i)}$, $k_{3(R_i,R_j)}$ $(= k_3$ at $R_iR_j \neq H)$ and k_4.

Later we will also use the terms

$$k_2 = \sum_{R_i} k_{2(R_i)} \frac{[R_i]}{[R]} \quad (R = \sum_{R_i} R_i) \tag{5}$$

and the mean value of the recombination constants k_3.

By means of a special analysis, made with consideration of the fact that in the reaction mixture the activity of the methane is much greater than the activities of the remaining gases, whereas the total concentration $[CH_4] << [M]$, and utilizing a number of experimental determinations,* gives the following expressions (the active products are designated by *) for the relationship between the concentrations of the various active products and the time t.

$$\Delta = [CH_4^\bullet]_0 - \alpha [CH_4^\bullet] =$$

$$= k_2 [CH_4^\bullet]_0 [R] t \frac{(1 + \bar{k}_3 t [R])}{1 + k_{2(CH_4)} [M] t + \bar{k}_3 [R] t}; \tag{6}$$

$$[C_2H_6^\bullet] = \frac{k_3 [CH_3] [CH_3^\bullet]}{1 + kt}; \tag{7}$$

$$[C_3^\bullet] = \frac{k_3 [CH_3^\bullet] [C_2H_5]}{1 + t f_{C_3}(t)}; \tag{8}$$

$$[C_4^\bullet] = \frac{k_3 [C_2H_5^\bullet] [CH_5]}{1 + t f_{C_4}(t)}, \tag{9}$$

where in the approximation used

$$[R] = \frac{1}{4 \bar{k}_3 t} \left[\sqrt{1 + 16 k_1 \bar{k}_3 t^2 [C_2H_6]} - 1 \right];$$

$$[CH_3^\bullet] = \frac{k_2 [CH_4^\bullet] [R] t}{1 + k_{2(CH_4)} [M] t + \bar{k}_3 t [R]};$$

$$[CH_3] = \frac{2k_1 [C_2H_6] t + k_2 [CH_4] [R] t}{1 + k_{2(CH_4)} [M] t + \bar{k}_3 t [R]}; \tag{10}$$

$$[C_2H_5] = \frac{k_2 [C_2H_6] [R] t}{(1 + k_{2(C_2H_4)} [M] t + \bar{k}_3 t [R]) + k_4 t},$$

---

* The experimental results mainly used by us were those that were in accord with the premise that the activity of C_3 exceeds the activity of all of the other products formed (Table 1) and that the decomposition of C_2H_6* is not the principal path for the formation of active ethylene. The character of the dependence of the various products on t was also taken into consideration.

while $f_{C_3}(t)$ and $f_{C_4}(t)$ designate the functions of $C_3^{\bullet}$ and $C_4^{\bullet}$ destruction, in which connection $[C_3^{\bullet}](1 + tf_{C_3}[t]) \cong$ $\cong [C_3^{\bullet}] + 2[C_2H_4^{\bullet}] + 2[C_4^{\bullet}] - 2kt[C_2H_6^{\bullet}]$.

Here the rate constant of the chain reaction k_c, proceeding through the elementary act (4), can be expressed in the form

$$k_c = \frac{k_4[C_2H_5]}{[C_2H_6]} = \frac{k_4 t \cdot k_2[R]}{1 + k_{2(C_2H_5)}[M]\,t + \bar{k}_3\,t\,[R]) + k_4 t}. \tag{11}$$

The obtained data permit finding directly the upper limit of k_c with the aid of the inequality

$$k_c < \frac{k_2 k_4 t\,[R]}{(1 + \bar{k}_3 t\,[R] + k_{2(CH_3)}\,[M]\,t} \leqslant \frac{[C_3^{\bullet}]}{[C_4^{\bullet}]}\;\frac{[C_2H_4^{\bullet}]}{t\,[CH_4^{\bullet}]}\,. \tag{12}$$

Substitution of the experimental values in (12) gives $k_c/k < \sim 0.05$ at 770 and $k_c/k < \sim 0.05$-0.1 at 890°. As a result, even a preliminary evaluation reveals that in the examined case the role played by chain reactions in the total cracking process is very small within the scope of the generally accepted scheme.

To determine the exact values of k_c and to establish the values of the elementary constants,it proves necessary to introduce additional thermodynamic considerations, connecting k_1 and k_3, in which connection it is sufficient to find the values of $k_1\bar{k}_3$, entering into the expression for [R]. The existing tabulated data for the thermodynamic functions [6] permits calculating the equilibrium constants* $K_I = (k'_1)^2/k_1k_3$ and $K_{II} = k_1/\bar{k}_3$, which are respectively equal to 0.10 and $1.8 \cdot 10^9$ at 770°; 4.6 and $2.4 \cdot 10^{10}$ at 840°; 70 and $1.13 \cdot 10^{11}$ at 890°.

On the assumption that only bimolecular recombination is present we can then substitute $k'_1 = 10^{13}e^{-101/RT}$. Then, by combining K_I and K_{II}, we find the value of k_3, equal to $7.1 \cdot 10^{-13}$ at 770°; $6 \cdot 10^{-13}$ at 840° and $4.5 \cdot 10^{-13}$ at 890°. Substitution of the indicated k_3 values in the expression for K_{II} gives values for k_1 that are those determined in study [7]. The value of k_3, obtained on the assumption of a double collision during recombination, possesses a steric factor of the order of 10^{-3} and differs but slightly from the standard value for a triple collision at the studied pressure; consequently, we took $k_1\bar{k}_3$ equal to $2.8 \cdot 10^{-16}$ at 770°, $2.14 \cdot 10^{-15}$ at 840° and $9.33 \cdot 10^{-15}$ at 890°. These values are obtained by substituting in K_1 the selected value of $k_1^{\prime}$ with a factor of $\sim {}^1/_3$. Combining the formulas given above, it then becomes possible to obtain from the experimental data the values of $k_{2(CH_3)}$, equal to $2.2 \cdot 10^{-16}$ at 770° and $4 \cdot 10^{-16}$ at 890°, which corresponds to an activation energy at 12 ± 2 kcal and a steric factor of the order of 10^{-3}.

The possibility of such small steric factors in reactions of the (2) type was indicated earlier [8, 9]. The values obtained for $k_2/\bar{k}_3$ are $2.8 \cdot 10^{-3}$ at 770° and $3.3 \cdot 10^{-2}$ at 890°. Such a large increase in the latter value should apparently be associated with an increase in the part played by H radicals. For the same reason the ratio $k_3/\bar{k}_3$ increases from approximately unity at 770° to 2.5 at 890°. In accord with the previous considerations, an estimate of k_3 from the experimental data gives a value of $\sim 5 \cdot 10^{-13}$. The value of the preexponent for k_4 proves to be 10^3 times smaller than the standard value. Substitution of the above-determined constants in Expression (4) gives for the ratio k_c/k a value of the order of 0.03.

In conclusion, the authors wish to thank V.V. Voevodsky and V.I. Vedeneev for their discussion of the problem.

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* The constants of the various recombination processes tend to equalize; the concentrations are expressed in molecules/cc.

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KINETICS OF THE ACID-CATALYZED DECARBONYLATION OF BENZOYLFORMIC ACID

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(Presented by Academician V.N. Kondratyev, June 17, 1957)

Although extensive literature exists on the nature of the elementary act of acid-catalyzed processes, still the mechanisms that have been advocated are most frequently based only on formal kinetics rules. In the present study an attempt was made to disclose the elements taking part in the elementary act of acid processes, and to compare the velocity constant with their concentration. As a model we selected the reaction for the decarbonylation of benzoylformic acid $C_6H_5COCOOH \rightarrow CO + C_6H_5COOH$. Elliott and Hammick [1] studied the kinetics of $C_6H_5COCOOH$ decarbonylation by the rate of CO evolution. They established that, with respect to $C_6H_5COCOOH$, the reaction is monomolecular, and that during the course of the process the rate constant, K, remains constant practically to complete decomposition. They studied the catalytic action of H_2SO_4 in a narrow range of acid concentration (from 94.05 to 98%). In this concentration interval the effective rate constant, K, is approximately proportional to the square of the acidity of the medium.

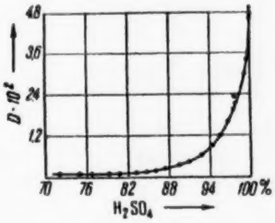


Fig. 1. Optical density of $C_6H_5COCOOH$ solutions in H_2SO_4, as a function of the H_2SO_4 concentration; T = 15°.

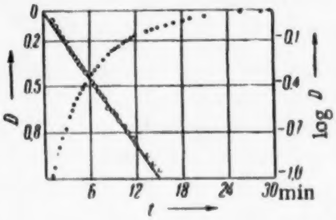


Fig. 2. Curve for the rate of $C_6H_5COCOOH$ decarbonylation by 99.94% H_2SO_4 and its logarithmic anamorphosis; T = 15°.

Solutions of benzoylformic acid in water and dilute sulfuric acid solutions do not absorb in the visible region of the spectrum. Absorption in the visible region of the spectrum appears when $C_6H_5COCOOH$ is dissolved in concentrated H_2SO_4 (80-90%); such a solution may be made colorless by diluting it with water. The absorption coefficient, for example ϵ^{400}, of a solution of benzoylformic acid in sulfuric acid shows a strong increase when the H_2SO_4 concentration is increased (cf. Figure 1).

In the present study the decarbonylation rate of $C_6H_5COCOOH$ in H_2SO_4 solutions was measured by the rate of decrease in the optical density of the solution at $\lambda = 400$ mμ. An SF-4 spectrophotometer was used to measure the optical density, using quartz cuvettes.

A typical kinetics curve of the decarbonylation process (the optical density of solution D is plotted as a function of the time t) and its logarithmic anamorphosis are shown in Figure 2.

The influence of the acidity of the medium h_0 on the value of K was investigated in the interval of H_2SO_4 concentrations ranging from 85.46 to 99.94%, at T = 15°. These data are shown in Table 1 and plotted in Fig. 3.

A linear relationship exists between log K and the acidity function H_0 in the acidity region ranging from $h_0 =$ $= 10^{8.06}$ to h_0 $10^{9.4}$: $\log K + 1.8\, H_0 = \text{const}$. A deviation from this relationship is observed at higher acidities, and in the region close to 100% H_2SO_4, the rate constant increases even slower than would be expected if a proportionality existed between log K and H_0. The dependence of K on the temperature was determined for solutions of $C_6H_5COCOOH$ in 98.80, 96.2, 92, 89.77 and 85.46% H_2SO_4, but in a narrow temperature range. As can be seen from Figure 4, these data fit into the Arrhenius equation, but it proves that the energy of activation determined in this manner is a function of the acid concentration.

TABLE 1

Expt. Nos.	H_2SO_4, %	H_0	K, min^{-1}	C_0	C_1	C_2	K/C_2
1	85.46	—8.06	$7.95 \cdot 10^{-6}$	0.97	$2.6 \cdot 10^{-2}$	$3.3 \cdot 10^{-5}$	0.24
2	89.77	—8.6	$8.32 \cdot 10^{-5}$	0.92	$8.5 \cdot 10^{-2}$	$3.7 \cdot 10^{-4}$	0.23
3	92.0	—8.9	$2.57 \cdot 10^{-4}$	0.84	0.16	$1.36 \cdot 10^{-3}$	0.2
4	94 34	—9.24	$1.17 \cdot 10^{-3}$	0.82	0.28	$5.4 \cdot 10^{-3}$	0.22
5	95.61	—9.43	$2.8 \cdot 10^{-3}$	0.61	0.38	$1.17 \cdot 10^{-2}$	0.24
6	96.2	—9.55	$3.75 \cdot 10^{-3}$	0.55	0.43	$1.62 \cdot 10^{-2}$	0.23
7	96.63	—9.60	$4.1 \cdot 10^{-3}$	0.51	0.47	$2\ 08 \cdot 10^{-2}$	0.2
8	96.74	—9.62	$5.2 \cdot 10^{-3}$	0.48	0.50	$2.24 \cdot 10^{-2}$	0.23
9	97.36	—9.74	$7.18 \cdot 10^{-3}$	0.42	0.54	$3.27 \cdot 10^{-2}$	0.22
10	97.39	—9.75	$7.57 \cdot 10^{-3}$	0.42	0.55	$3.38 \cdot 10^{-2}$	0.22
11	97.76	—9.83	$9.67 \cdot 10^{-3}$	0.38	0.58	$4.27 \cdot 10^{-2}$	0.23
12	97.82	—9.85	$11.5 \cdot 10^{-2}$	0.36	0.60	$4.6 \cdot 10^{-2}$	0.25
13	98.18	—9.92	$1.46 \cdot 10^{-2}$	0.32	0.62	$5.7 \cdot 10^{-2}$	0.26
14	98.80	—10.02	$2.64 \cdot 10^{-2}$	0.24	0.67	$9 \cdot 10^{-2}$	0.29
15	99.18	—10.21	$3.93 \cdot 10^{-2}$	0.19	0.69	0.12	0.33
16	99.47	—10.38	$7.09 \cdot 10^{-2}$	0.12	0.7	0.18	0.39
17	99.90	—10.83	$14.4 \cdot 10^{-2}$	0.03	0.56	0.41	0.35
18	99.94	—10.93	0.16	0.03	0.52	0.45	0.36

Note: The values of K for 85.46, 89.77 and 92% H_2SO_4 were obtained by extrapolation from the rates at high temperatures.

Based on the fact that solutions of $C_6H_5COCOOH$ in concentrated and dilute H_2SO_4 solutions differ in color, it can be concluded that in these media the benzoylformic acid is found in different forms. There is reason to believe that the $C_6H_5COCOOH$, dissolved in dilute H_2SO_4, is found in the nonionized state, and that it suffers ionization (protonization) when the acidity of the medium (acid concentration) is increased. In 72% and more dilute solutions $\epsilon = 7.0$ at $\lambda = 400$ mμ. We take this value as the absorption coefficient of the nonionized form of benzoylformic acid.

To determine the basicity constant it is necessary to know, in addition to ϵ_0, the absorption coefficient of the ionized form ϵ_1 and the acidity function H_0 of the medium. The values of H_0 for H_2SO_4 solutions at 15° were measured by us. If the optical densities $D = \epsilon_0 C_0 + \epsilon_1 C_1$ in solutions with a different acidity are known, then ϵ_1 is determined from the equation

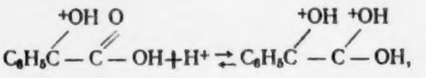
$$\Delta H_0 = \log \frac{D_1 - \epsilon_1}{D_2 - \epsilon_2} + \log \frac{D_2 - \epsilon_0}{D_1 - \epsilon_0}, \tag{1}$$

where ΔH_0 is the difference in the acidity functions of solutions with optical densities D_1 and D_2. Having determined ϵ_1, we can then calculate the pK_1 value of the reagent.

In determining ϵ_1 we encountered the following fact. If the values of D in the concentration interval of 90 to 96% H_2SO_4 are used, then the average value of ϵ_1, calculated from Equation (1), is equal to $2.95 \cdot 10^2$ and $pK_1 = -9.63$. Actually, at H_2SO_4 concentrations close to 100%, the optical densities of $C_6H_5COCOOH$ are higher than would be expected by extrapolation from the values of pK_1, calculated in the interval from 90 to 96% H_2SO_4 (for example, at $C_{H_2SO_4} = 99.94\%$, $D = 4.7 \cdot 10^2$). If ϵ_1 is determined from the values of D in the interval $C_{H_2SO_4} = 95$ to 99.94%, then $\epsilon^{400} = 53$. Such a difference in the values of ϵ_1 cannot be explained by an error in the measurements. It is our belief that the appearance of excess optical density at $\lambda = 400$ mμ for solutions of $C_6H_5COCOOH$ in H_2SO_4 at concentrations above 95% is associated with the appearance of substantial concentrations of a new form – a twice protonized benzoylformic acid. Ionization of the type

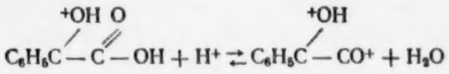
$$RCOCOOH + H^+ \rightleftarrows RCOCO^+ + H_2O \qquad (2)$$

cannot be assumed for the first protonization of $C_6H_5COCOOH$. If Scheme (2) is adopted, then the values of ϵ obtained for the ionized form are slightly too low and the experimentally observed large values of ϵ at high acidities cannot be explained. The second protonization can proceed either by the scheme



$$C_6H_5\overset{+OH}{C}-\overset{O}{C}-OH + H^+ \rightleftarrows C_6H_5\overset{+OH}{C}-\overset{+OH}{C}-OH, \qquad (3)$$

or by the scheme



$$C_6H_5\overset{+OH}{C}-\overset{O}{C}-OH + H^+ \rightleftarrows C_6H_5\overset{+OH}{C}-CO^+ + H_2O \qquad (4)$$

When the decrease in the concentration of the once ionized form with increase in h_0 is taken into account, log K will be a linear function of H_0 in the case of ionization by Scheme (3) and a function of I_0 in the case of ionization by Scheme (4). In accord with our experimental data, log K is a linear function of H_0 when variation in C_1 is taken into account. The value $pK_1 = -9.63$, determined in the H_2SO_4 concentration interval of 90 to 96%, we attribute to the once protonized form. The absorption coefficient ϵ_2 and pK_2 of the twice ionized form can be calculated from the equations

$$D = \varepsilon_0 C_0 + \varepsilon_1 C_1 + \varepsilon_2 C_2; \; H_0 = pK_2 + \log \frac{C_1}{C_2}, \qquad (5)$$

where the once ionized form is the principal one.

Using Equations (5) and the values of D in the H_2SO_4 concentration interval of 97 to 99.94% we calculated $\epsilon_2 = 0.95 \cdot 10^3$ and $pK_2 = -10.96$.

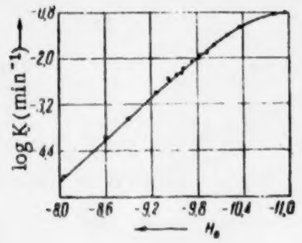


Fig. 3. Log K as a function of the acidity H_0 at T = 15°.

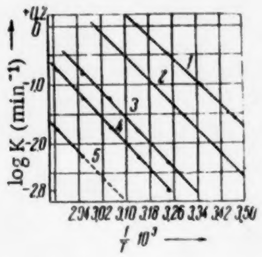
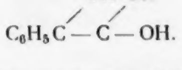


Fig. 4. Relationship between the temperature and the rate constant for the decarbonylation of benzoylformic acid at various H_2SO_4 concentrations: 1) C = = 98.56%, E = 22.1 kcal/mole; 2) C = 96.2%, E = 22.7 kcal/mole; 3) C = 92%, E = 25.2 kcal/mole; 4) C = 89.77%, E = 25 kcal/mole; 5) C = 85.46%, E = 25 kcal/mole.

Consequently, in our opinion, $C_6H_5COCOOH$ exists in three forms in sulfuric acid: as the nonionized form (C_0), as the once protonized (C_1), and as the twice protonized form (C_2).

The values of pK_1 and pK_2 were used to calculate the relative concentrations C_0, C_1 and C_2 as a function of the acidity of the medium. Which of these forms of $C_6H_5COCOOH$ is reactive? It is natural for the unprotonized form to be unreactive. The once protonized form is also incapable of reaction, since a linear proportionality between the rate constant K and C_1 is not observed. As can be seen from Table 1, in the interval of change in K from $8 \cdot 10^{-6}$ to 0.16 min^{-1} the ratio K/C_2 is nearly constant. On the basis of this we assume that it is the twice ionized form that participates in the limiting act of the decarbonylation of benzoylformic acid.



$$C_6H_5\overset{+OH}{C}-\overset{+OH}{C}-OH.$$

To derive the equation for the rate of the process we will designate the equilibrium constant of the first protonization $B + H^+ \rightleftharpoons BH^+$ by

$$K_1 = \frac{a_{BH^+}}{a_B a_{H^+}} = \frac{C_{BH^+}}{C_B a_{H^+}} \frac{f_{BH^+}}{f_B} = \frac{C_{BH^+}}{C_B} \frac{1}{h_0} \qquad (6)$$

and the equilibrium constant of the second protonization $BH^+ + H^+ \rightleftharpoons BH_2^{++}$ by

$$K_2 = \frac{a_{BH_2^{++}}}{a_{BH^+} a_{H^+}} = \frac{C_{BH_2^{++}}}{C_{BH^+} a_{H^+}} \frac{f_{BH_2^{++}}}{f_{BH^+}} = \frac{C_{BH_2^{++}}}{C_{BH^+}} \frac{1}{h_+}. \tag{7}$$

Using the balance equation $C_0 + C_1 + C_2 = C$ and Relationships (6) and (7), we obtain the general expression for the concentration of the twice ionized form $C_{BH_2^{++}} = \frac{K_1K_2h_0h_+}{1 + K_1h_0 + K_1K_2h_0h_+} C$. Assuming that the BH_2^{++} molecules are found in equilibrium with the activated $(BH_2^{++})^*$ complex, then the equation for the rate of the process can be written as:

$$-\frac{dC}{dt} = W = K'_{true} \frac{a_{(BH_2^{++})^*}}{f_{(BH_2^{++})^*}} = K_{true} \frac{C_{BH_2^{++}} f_{BH_2^{++}}}{f_{(BH_2^{++})^*}}. \tag{8}$$

In the given process the composition of the activated $(BH_2^{++})^*$ complex is the same as that of the twice protonized BH_2^{++} molecule. Consequently, full basis exists to assume that the activity coefficients of the activated complex $f_{(BH_2^{++})^*}$ and the twice protonized molecule $f_{(BH_2^{++})}$ are equal. Assuming $f_{BH_2^{++}} = f_{(BH_2^{++})^*}$, we obtain

$$-\frac{dC}{dt} = K_{true} C_{BH_2^{++}} = K_{true} \frac{K_1K_2h_0h_+}{1 + K_1h_0 + K_1K_2h_0h_+} C = KC; \tag{9}$$

K_{true} is the true rate constant.

As can be seen from Equation (9), if several equilibrium forms of the reacting substance are present in the case of a monomolecular process the experimentally determined rate constant K is the effective one. The effective constant represents the product of the true rate constant multiplied by the fraction of reactive molecules to the total number of molecules of the reacting substance. Only in the case where all of the molecules of the reacting substance are found in the reactive form (in our case in the form of BH_2^{++}) does the determined rate constant become the true one. Since larger $C_{BH_2^{++}}$ concentrations (0.4C) are attained at H_2SO_4 concentrations of ~99.94%, then the energy of activation at such acidities (E = 21.8 kcal/mole) can be assumed to be the true value.

Taking E_{true} = 21.8 kcal/mole, we calculated the preexponent of the process; this value is equal to $1.5 \cdot 10^{14}$, which is close to the normal values of preexponents for monomolecular processes.

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MOLECULAR ORBITS OF SYSTEMS COMPOSED OF CONDENSED FIVE-, SIX- AND SEVEN-MEMBERED RINGS

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(Presented by Academician I.I. Chernyaev, June 29, 1957)

One of the major achievements of quantum chemistry was the prediction that the C_5H_5 cycle, having one free position on a useful molecular orbit (MO), should be stable as a singly-charged anion, and that the C_7H_7 cycle, having only three useful MO, on which only 6 π-electrons can find room,should be stable in the form of a singly-charged cation. These predictions were confirmed by obtaining the $C_5H_5^-$ anion (for example, in C_5H_5Na, $(C_5H_5)_2Mn$, etc.) and the tropylium cation $C_7H_7^+$ [2]. Recently, a communication appeared on the synthesis of a stable carbonium cation composed of three condensed six-membered rings (V in Table 1 [3]), in which connection the possibility of this cation existing was predicted earlier on the basis of the calculations made by Dewar and Pettit [4] employing the MO method, which led to the conclusion that such a cation would be quite stable.

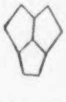
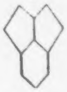
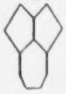
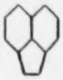
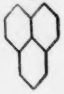
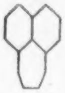
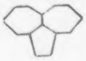
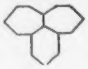
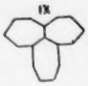
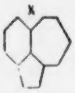
In connection with this we became interested in the problem of the MO of systems composed of three condensed rings, including five- and seven-membered cycles, and we calculated the energies of the MO of such systems by the usual MO method as an approximation of LCAO. The calculation results, expressed in terms of coulomb integrals C and resonance integrals β, are presented in Table 1, where the energies of all of the useful MO and two of the lower unprofitable MO are also given. Our calculations support the conclusion made by Dewar and Pettit relative to system V, since in this system there exist 6 useful MO for 12 electrons, while the 13th π-electron should be found on an orbit, the exchange energy of which is equal to zero, so that easy cleavage of this electron could be expected, since the energy of the occupied MO is sufficient to assure stability for the system $C_{13}H_{13}^+$ ($12C + 17.82\beta$).

As calculation shows, in the systems III, IV, VI and VII the number of useful MO is equal to the number of available pairs of π-electrons, so that such systems should exist in the form of neutral molecules, in accord with the possibility of writing for them structural formulas with double bonds and with all of the tetravalent C atoms.

Further, we found that in system II with 11 π-electrons there exist 6 useful MO, so that such a condensed system should possess the tendency to add an extra electron with the formation of $C_{11}H_{11}^-$. It is interesting to mention that in the case of pentalene such a tendency does not exist (it has 4 useful MO and 8 π-electrons), and that the condensation of the third six-membered ring to naphthalene in V also does not lead to the appearance of a free position on a useful MO, so that the presence of such a free position is a specific trait inherent to system II, composed of two five-membered cycles and one six-membered cycle. The reverse is true for system VIII, in which only 7 useful MO and 15 π-electrons are present, so that the $C_{16}H_{16}$ cycle, the same as the tropylium ion, should be stable in the form of a singly-charged cation. System VIII also differs from the system composed of two condensed seven-membered rings ("heptalene"), in which 5 useful MO and one MO with zero exchange energy are present. The results obtained for systems I and IX seem to be the most interesting to us. For the first of them we found 6 useful MO, since the number of π-electrons is equal to 10. This means that, for the $C_{10}H_{10}$ (I) cycle, the tendency could be expected to add 2 extra electrons with the formation of a doubly-charged anion. To be sure, it should be mentioned that the addition of 2 extra electrons may be difficult due to their repulsion. On the other hand, in the case of IX there are 16 π-electrons and only 7 useful MO present, so that such a system should strive to release 2 electrons with transition into a doubly-charged cation. Since hindrances, associated with electron repulsion, are not present in this case, we postulate that such a condensed system com-

TABLE 1

Energies of Molecular Orbits

I 	II 	III 	IV 	V 
C + 2.52 β C + 1.53 β C + 1.53 β C + 0.57 β C + 0.35 β C + 0.35 β	C + 2.49 β C + 1.62 β C + 1.62 β C + 0.81 β C + 0.62 β C + 0.46 β	C + 2.48 β C + 1.71 β C + 1.68 β C + 1.00 β C + 0.83 β C + 0,48 β	C + 2.47 β C + 1.68 β C + 1.68 β C + 1.00 β C + 0,83 β C + 0.64 β	C + 2,45 β C + 1.73 β C + 1,73 β C + 1.00 β C + 1,00 β C + 1.00 β
C − 1.00 β C − 1.88 β	C − 0.62 β C − 1.21 β	C − 0.28 β C − 0.59 β	C − 0.28 β C − 1,00 β	C C − 1.00 β C − 1.00 β
Number of electrons 10	11	12	12	13
VI 	VII 	VIII 	IX 	X 
C + 2.43 β C + 1.77 β C + 1.77 β C + 1.21 β C + 1,13 β C + 1.00 β C + 0,24 β	C + 2,45 β C + 1.79 β C + 1.77 β C + 1.30 β C + 1.13 β C + 0.76 β C + 0.24 β	C + 2.42 β C + 1.80 β C + 1.80 β C + 1,33 β C + 1.24 β C + 1.10 β C + 0.45 β	C + 2,41 β C + 1.83 β C + 1,83 β C + 1,34 β C + 1.34 β C + 1.30 β C + 0.62 β	C + 2.54 β C + 1 74 β C + 1,72 β C + 1.18 β C + 1.00 β C + 0.68 β C
C − 0.46 β C − 0.71 β	C − 0.33 β C − 0.71 β	C − 0.31 β C − 0.45 β	C − 0.21 β C − 0.21 β	C − 0.51 β C − 1.00 β
Number of electrons 14	14	15	16	13

posed of 3 seven-membered rings should exist in the form of the salt $[C_{16}H_{16}]^{2+}X^{2-}$.

The character of the MO in system X is the same as in system V.

The authors consider it their pleasant duty to thank M.E. Volpin, who brought this problem to our attention.

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ADSORPTION OF VAPORS IN THE FORMATION ON THE SURFACE OF COMPLEXES FROM MOLECULES OF THE ADSORBATE

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(Presented by Academician M.M. Dubinin, June 27, 1957)

Together with the polymolecular adsorption of vapors, described well by the BET equation at large adsorption energies, where the interactions between the adsorbate molecules can be neglected [1, 2], there are many cases where interaction of the adsorbed molecules plays a major role, leading to the formation of complexes on the surface; in the case of water the molecules in these complexes are connected by hydrogen bonds [3-5]. In this connection, it seems of interest to examine the adsorption of a vapor, taking into account the distribution of the complexes of the adsorbatate molecules both perpendicular to the surface and along it.

A distribution of the complexes along the surface after localization of the molecules at the primary active centers was discussed in studies [4-9]. However, in cases similar to the adsorption of water vapors on graphitized carbon blacks such centers are absent. Consequently, we will examine here the case of the adsorption of a vapor on a homogeneous surface, not bearing any specific centers for the given adsorbate. Here, the same as in the case of the BET formula, we will examine the general case of van der Waals forces in the surface layer.

We will use the method of quasichemical equilibria, which was used by us in the thermodynamical derivation of the BET equation [1]. We will examine the chain of quasichemical reactions:

1. Primary Reaction of the Formation of Single Complexes:

molecule of the vapor + free surface ⇌ single complex

The equilibrium constant is [1]

$$K_1 = \theta_1/p\theta_0 \quad \text{or} \quad K_1' = \theta_1/h\theta_0, \tag{1}$$

where θ_1 is the portion of the surface occupied by a single complex; θ_0 is the portion of the free surface; p is the pressure of the vapor; $h = p/p_s$ is the relative pressure of the vapor, and $K_1' = K_1p_s$.

2. Formation of Multiple Complexes Along the Surface:

single complex + single complex ⇌ double horizontal complex

single complex + double horizontal complex ⇌ triple horizontal complex, etc.*

The constants of these equilibria are

$$K_2 = \theta_2/\theta_1\theta_1; \quad K_3 = \theta_3/\theta_1\theta_2, \ldots, \tag{2}$$

where $\theta_2, \theta_3, \ldots$ are the portions of the adsorbent surface occupied by double, triple, etc. horizontal complexes.

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* We neglect the possibility of forming multiple complexes from multiple complexes.

Strictly speaking, these constants are dissimilar, since both the energy and entropy of adsorption depend on the coordination. However, taking this relationship into consideration introduces a new constant [6]. Consequently, by analogy with the assumption in the BET equation for vertical complexes [10], we will assume that

$$K_2 \approx K_3 \approx \ldots = K_n. \tag{3}$$

If the adsorption remains monomolecular, i.e., vertical complexes are not formed, then the total degree to which the monolayer is filled, in accord with (1) and (2) under the conditions of (3), is:

$$\theta' = \frac{\alpha}{\alpha_m} = \theta_1 + \theta_2 + \theta_3 + \ldots =$$

$$= \theta_1 [1 + K_n\theta_1 + (K_n\theta_1)^2 + \ldots] = \frac{\theta_1}{1 - K_n\theta_1} \tag{4}$$

[expressing the corresponding sum of the terms of the geometric progression by $1/(1 - K_n\theta_1)$].* Taking θ_1 from (1) and substituting $\theta_0 = 1 - \theta'$, we obtain

$$\theta' = \frac{K_1' h (1 - \theta')}{1 - K_n K_1' h (1 - \theta')} \tag{5}$$

or

$$\alpha = \frac{\alpha_m K_1' h (1 - \alpha/\alpha_m)}{1 - K_n K_1' h (1 - \alpha/\alpha_m)}. \tag{6}$$

The obtained adsorption isotherm equation is solved for h

$$h = \frac{\theta'}{K_1' (1 - \theta')(1 + K_n\theta')}. \tag{7}$$

In linear form it has the appearance

$$\theta'/h(1 - \theta') = K_1' + K_n K_1' \theta'. \tag{8}$$

Equations (5), (6) and (7) contain three constants: α_m, K'_1 and K_n, and consequently to determine K'_1 and K_n in the general case it is necessary to find α_m independently.

In the absence of association, i.e., at $K_n \approx 0$, this equation converts into the Langmuir equation $\alpha = \alpha_m K'_1 h/(1 + K'_1 h)$. For strongly adsorbed substances ($K'_1 \gg 1$) large values of θ' are attained even at small values of h, and consequently the product $h(1 - \theta')$ is small for all values of θ', so that for all practical purposes the equation converts into the Langmuir equation, i.e., it describes a convex isotherm, and also for $K_n > 0$.

With reduction in K'_1 isotherm (5) is expressed by an S-shaped curve – it is concave at first, then passes through an inflection point, and finally approaches the limit. In this case, it is already impossible to neglect the formation of vertical complexes at small values of K'_1.

3. Formation of vertical complexes. We will assume the approximation that the appearance of vertical complexes does not change the horizontal interactions in the first layer,** so that the adsorption in the first layer is expressed by Equations (5) and (6). Vertical complexes of variable multiplicity build up on top of the horizontal complexes.

a) The formation of double vertical complexes occurs on that portion of θ' that does not bear any multiple vertical complexes. We will designate this free portion over θ' by θ'_0. Then, from [1], for a quasichemical reaction:

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*α is the magnitude of adsorption, and α_m is the magnitude of adsorption in a dense monolayer.

**Later it will be necessary to take this effect into consideration, and also the horizontal interactions in each layer, leading, at times, to wavelike adsorption isotherms.

molecules of the vapor + complexes of the first layer uncovered on top $\rightleftharpoons$
$\rightleftharpoons$ double vertical complexes

$$K'' = \theta''/h\theta'_0, \tag{9}$$

where θ'' is the portion of the surface corresponding to all of the double vertical complexes.

b) The formation of triple, quadruple, etc. vertical complexes:

molecules of the vapor + double vertical complexes $\rightleftharpoons$
$\rightleftharpoons$ triple vertical complexes, etc.

The constants of these equilibria are

$$K''' = \theta'''/h\theta''; \quad K'''' = \theta''''/h\theta'''; \ldots \tag{10}$$

We will assume,* the same as in the derivation of the BET equation, that

$$K'' \approx K''' \approx \ldots \approx K_l. \tag{11}$$

The total adsorption is equal to the sum of the adsorption values in the vertical complexes of each type [10], i.e.,

$$\begin{aligned} \alpha &= \alpha_m(\theta'_0 + 2\theta'' + 3\theta''' + \ldots) = \\ &= \alpha_m\theta'_0[1 + 2K_l h + 3(K_l h)^2 + \ldots]. \end{aligned} \tag{12}$$

Further, from a determination of θ'_0 and from (9), (10) and (11):

$$\begin{aligned} \theta' &= \theta'_0 + \theta'' + \theta''' + \ldots = \\ &= \theta'_0\{1 + K_l h[1 + K_l h + (K_l h)^2 + \ldots]\} = \frac{\theta'_0}{1 - K_l h}. \end{aligned} \tag{13}$$

The sum in the brackets in (12) is the derivative of the sum in the brackets in (13) [10], and consequently, the total degree of filling, taking (13) into consideration, is

$$\theta = \frac{\alpha}{\alpha_m} = \frac{\theta'_0}{(1 - K_l h)^2} = \frac{\theta'}{1 - K_l h} = \frac{\theta'}{1 - h} \tag{14}$$

($K_l = 1$, for the reason that at $h = 1$, $\alpha = \infty$). As a result, $\theta' = \theta(1 - h)$, where θ' represents the adsorption in the first layer of (5) and (6). Consequently, the equation for polymolecular adsorption, with the formation of horizontal complexes taken into account, assumes the appearance

$$\theta(1 - h) = \frac{K'_1 h[1 - \theta(1 - h)]}{1 - K_n K'_1 h[1 - \theta(1 - h)]}, \tag{15}$$

or, in linear form

$$\frac{\theta(1 - h)}{h[1 - \theta(1 - h)]} = K'_1 + K_n K'_1 \theta(1 - h). \tag{16}$$

This equation describes polymolecular adsorption isotherms with both a convex and concave initial portion (with one and with two inflection points). At $K_n \approx 0$ it converts into the equation with a convex initial portion

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*As an approximation, since the contribution of the adsorbent field to the energy of adsorption decreases in measure with its removal from the surface, i.e., in measure with the growth of the vertical complex. This makes the derivation inaccurate at large values of h, the same as in the case of the BET equation [1].

$$\theta = \frac{K_1' h}{(1-h)(1+K_1' h)}; \quad \frac{h}{\alpha(1-h)} = \frac{1}{\alpha_m K_1'} + \frac{1}{\alpha_m} h. \tag{17}$$

This equation coincides with the BET equation if $K'_1 \gg 1$, i.e., for substances that are strongly adsorbed. For weakly adsorbed substances (small K'_1, large K_n) θ still remains small at large values of h, and consequently, (17) converts into

$$\theta(1-h) \approx \frac{K_1' h}{1 - K_n K_1' h}, \quad \frac{h}{\alpha(1-h)} \approx \frac{1}{\alpha_m K_1'} - \frac{K_n}{\alpha_m} h, \tag{18}$$

i.e., it adjusts to the coordinates of the BET equation, but with a negative slope.

The presented description of the adsorption of vapors with the formation of both vertical and horizontal complexes is an approximation, since it contains assumptions (3) and (11). Actually, both the energy and entropy of adsorption depend on the coordination of the molecules in the complexes. This also holds for the completion of adsorption in each layer, which can be associated with an increased energy.

Of major interest is the case where the isotherm, concave at the start, passes through two inflection points, for example, in the adsorption of methanol and methylamine vapors on graphitized carbon black [3, 11, 12]. Equation (15) describes these cases well. Isotherms of this type were described in study [13] by statistical thermodynamics methods on the basis of assuming a localized layer with appropriate selection of the constants. Monomolecular adsorption isotherms with adsorbate-adsorbate interactions taken into account can be described on the basis of a two-dimensional analog of the van der Waals equation [14].* A comparison of the various equations for the isotherms of mono- and polymolecular adsorption with experiment will be made in the next communication.

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* The equation of state

$$\pi\omega = kT(1 + B_1/\omega + B_2/\omega^2 + \ldots), \tag{19}$$

where π is the two-dimensional pressure, ω is the area, occupied by an adsorbate molecule in a monolayer, and B_1 and B_2 are coefficients, corresponds to the adsorption isotherm Equation (5).

Equation (5) is also obtained by introducing the activity coefficients in (1), if it is assumed that their dependence on θ' is expressed by a linear function in the exponent and this function is decomposed into a series terminating in a linear term.

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KINETICS OF THE REACTION OF SODIUM WITH WATER AND THE SYSTEMS: WATER–DIOXANE AND WATER–BUTYRIC ACID

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(Presented by Academician P.A. Rebinder, June 22, 1957)

In investigating the rate of solution of sodium metal in benzene solutions of butyric acid it seemed of interest to study the effect of water on the course of this process. However, before studying the reaction of sodium with the systems composed of benzene-butyric acid-water it was first necessary to determine how sodium reacts with water alone, and then with the systems composed of water-butyric acid. The present paper is devoted to the results obtained in these investigations.

Water, due to its extremely rapid rate of reaction with sodium, was diluted with dioxane, which, as previous experiments had revealed, does not react with sodium at room temperature, or at least not with the evolution of hydrogen. In the systems composed of water and butyric acid, the role of a unique "diluent" for water was played by the acid.

The experimental procedure remained the same as before [1], with the only difference that in studying the reaction of sodium with water and the aqueous dioxane systems the tubes, in which the sodium was contained, were taken of smaller diameter (~ 1 mm) so as to reduce even more the surface area of contact between the metal and the solution. In this connection we had been convinced earlier that such a contraction in the opening of the tubes does not interfere with a uniform reaction course, as is evidenced by the curves shown in Figure 1.

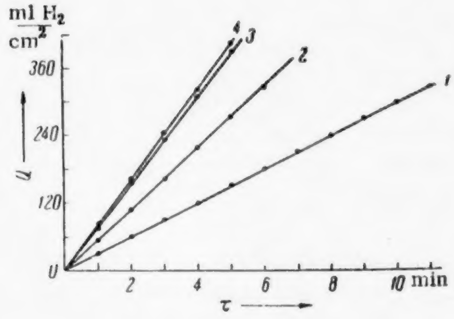

Fig. 1. Curves for the solution of sodium in water-dioxane systems. Q is the volume of hydrogen evolved in milliliters (reduced to standard conditions) from 1 cm^2 of sodium surface. The figures on the curves refer to the numbers of the systems.

The experiments were run at 20°. The weight of sodium was ~3 mg; a microburette served as the eudiometer. The water had been distilled twice. The 1,4-dioxane was Kahlbaum quality, purified by repeated freezing, with b.p. 100.8° and m.p. 11°; d_4^{20} 1.035; judging by the values of these constants the dioxane was practically anhydrous. The n-butyric acid [1] was chemically pure, with b.p. 162° and d_4^{20} 0.9640. The sodium [1] was also chemically pure, but it did contain traces of potassium.

We will present the composition of the studied systems.

The reaction with pure water was ended in a matter of several seconds (1 sec at 20° and 3 sec at 4°), which made visual observation of the reaction course very difficult. Consequently, most of the experiments were run with the water-dioxane systems. The data, characterizing the relationship between the reaction rate and the concentration of water in such systems, are plotted in Figure 2.

From these data it follows that the rate of reaction in systems Nos. 1-4 is a linear function of the concen-

Water-Dioxane

System No.	1	2	3	4	5
Concentration of water in mole parts $\cdot 10^3$	330	500	700	750	830

Water-Butyric Acid

System No.	1	2	3	4	5	6	7	8
Concentration of water in mole parts $\cdot 10^3$	0	1.0	2.0	4.0	8.0	16	31	62

System No.	9	10	11	12	13	14	15
Concentration of water in mole parts $\cdot 10^3$	111	204	333	500	667	750	800

System No.	16	17	18	19	20	21
Concentration of water in mole parts $\cdot 10^3$	833	875	900	909	923	1000

tration of water in them, and as a result obeys the equation for a first-order reaction $dC/dt = kC$, with a constant equal to $4.7 \cdot 10^{-5}$. With transition from system 4 to system 5 the reaction rate rises sharply, reaching values that are close to the value of the rate in pure water. The order of the reaction also changes, approaching that of zero order, characteristic for the reaction of sodium with pure water, and water-dioxane systems with a constantly diminishing amount of dioxane.

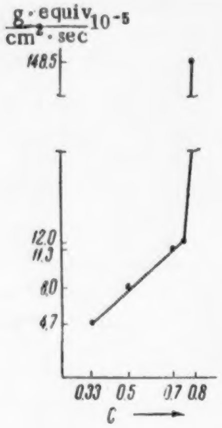

Fig. 2. Solution rate of sodium as a function of the concentration of water in water-dioxane systems.

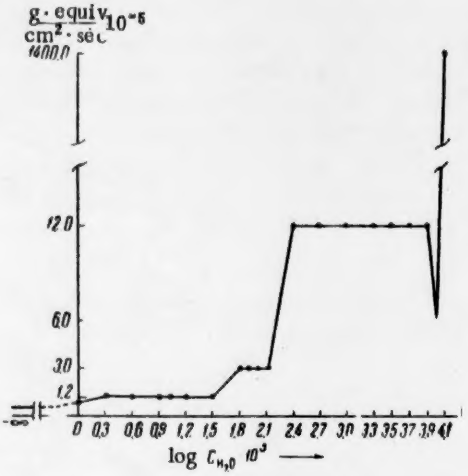

Fig. 3. Solution rate of sodium in butyric acid-water systems as a function of the concentration of water in them.

In all probability, dioxane forms with water, by means of hydrogen bonds, a series of oxonium compounds [2], and in that way inactivates the water to a certain degree. A sharp increase in the reaction rate, observed in the transition from system 4 to system 5, can, in such case, be due to a corresponding sharp increase in the concentration of "free" water, making its amount predominant over the amount of "bound" water. The increase in the value of the energy of activation in the transition from pure water to water-dioxane systems is apparently an argument in support of such a postulation.

As was revealed by measuring the reaction rate of water with sodium at 4, 14 and 24°, the apparent energy of activation of the reaction is 6 kcal/mole,* while for the reaction of sodium with water-dioxane system No. 1 (based on measurement of the rate at 20,30 and 40°) it is equal to 14.5 kcal/mole. As is known, the energy of a hydrogen bond lies in the limits 6-8 kcal/mole.

The solution rate of sodium in butyric acid-water systems as a function of the water content is depicted in Figure 3, showing a peculiar "steplike" character. The graph consists of a number of "steps," parallel to the abscissa, corresponding to a certain range of molar ratios of water and butyric acid, within the limits of which the solution rate of sodium remains constant, obeying the equation for a zero-order reaction. In this connection, the "steps" differ among themselves both as regards their length and height, i.e., they differ as regards the "jumps" in the rate in climbing from one "step" to another. Also no less strange is the drop in the rate (checked repeatedly) which is observed after the third step and precedes the last sharp rise in the reaction rate, where the values of the rate approach the value characteristic for the reaction with pure water.

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*According to the data of Deal and Svec [3] the E of the reaction between lithium metal and water vapors, depending on the pressure of the vapors, ranged from 6.2 to 5.5 kcal/mole.

The question naturally arises of the nature of such a strange kinetics rule and of the mechanism of the "steplike" effect. Judging from the fact that this effect is not observed when sodium metal is reacted with water alone or with butyric acid alone, it must be concluded that it appears as the result of the joint action of both these reagents on the metal. If now it is assumed that water and butyric acid do not enter into some sort of reaction with each other, then it is probable that in the first phase it is the water that reacts with the sodium, since the "apparent" energy of activation of this reaction is 6 kcal/mole, while for the reaction with butyric acid (dissolved in benzene) it is 13.5 kcal/mole.* However, the postulation intrudes that butyric acid forms with water, as the result of hydrogen bonding, a number of molecular compounds. It is specifically in the formation of such compounds, playing a preeminent role in the kinetics of the reaction with sodium, that, in our opinion, the key to solving the manifested kinetics rules should be sought.

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*The amount of water in the system, corresponding to the first point of the first step, is already sufficient for conversion of all of the sodium metal into its hydrate.

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